This is a digital copy of a book that was preserved for generations on library shelves before it was carefully scanned by Google as part of a project to make the world's books discoverable online.

It has survived long enough for the copyright to expire and the book to enter the public domain. A public domain book is one that was never subject to copyright or whose legal copyright term has expired. Whether a book is in the public domain may vary country to country. Public domain books are our gateways to the past, representing a wealth of history, culture and knowledge that's often difficult to discover.

Marks, notations and other marginalia present in the original volume will appear in this file - a reminder of this book's long journey from the publisher to a library and finally to you.

Usage guidelines

Google is proud to partner with libraries to digitize public domain materials and make them widely accessible. Public domain books belong to the public and we are merely their custodians. Nevertheless, this work is expensive, so in order to keep providing this resource, we have taken steps to prevent abuse by commercial parties, including placing technical restrictions on automated querying.

We also ask that you:

+ *Make non-commercial use of the files* We designed Google Book Search for use by individuals, and we request that you use these files for personal, non-commercial purposes.

+ *Refrain from automated querying* Do not send automated queries of any sort to Google's system: If you are conducting research on machine translation, optical character recognition or other areas where access to a large amount of text is helpful, please contact us. We encourage the use of public domain materials for these purposes and may be able to help.

+ *Maintain attribution* The Google "watermark" you see on each file is essential for informing people about this project and helping them find additional materials through Google Book Search. Please do not remove it.

+ *Keep it legal* Whatever your use, remember that you are responsible for ensuring that what you are doing is legal. Do not assume that just because we believe a book is in the public domain for users in the United States, that the work is also in the public domain for users in other countries. Whether a book is still in copyright varies from country to country, and we can't offer guidance on whether any specific use of any specific book is allowed. Please do not assume that a book's appearance in Google Book Search means it can be used in any manner anywhere in the world. Copyright infringement liability can be quite severe.

About Google Book Search

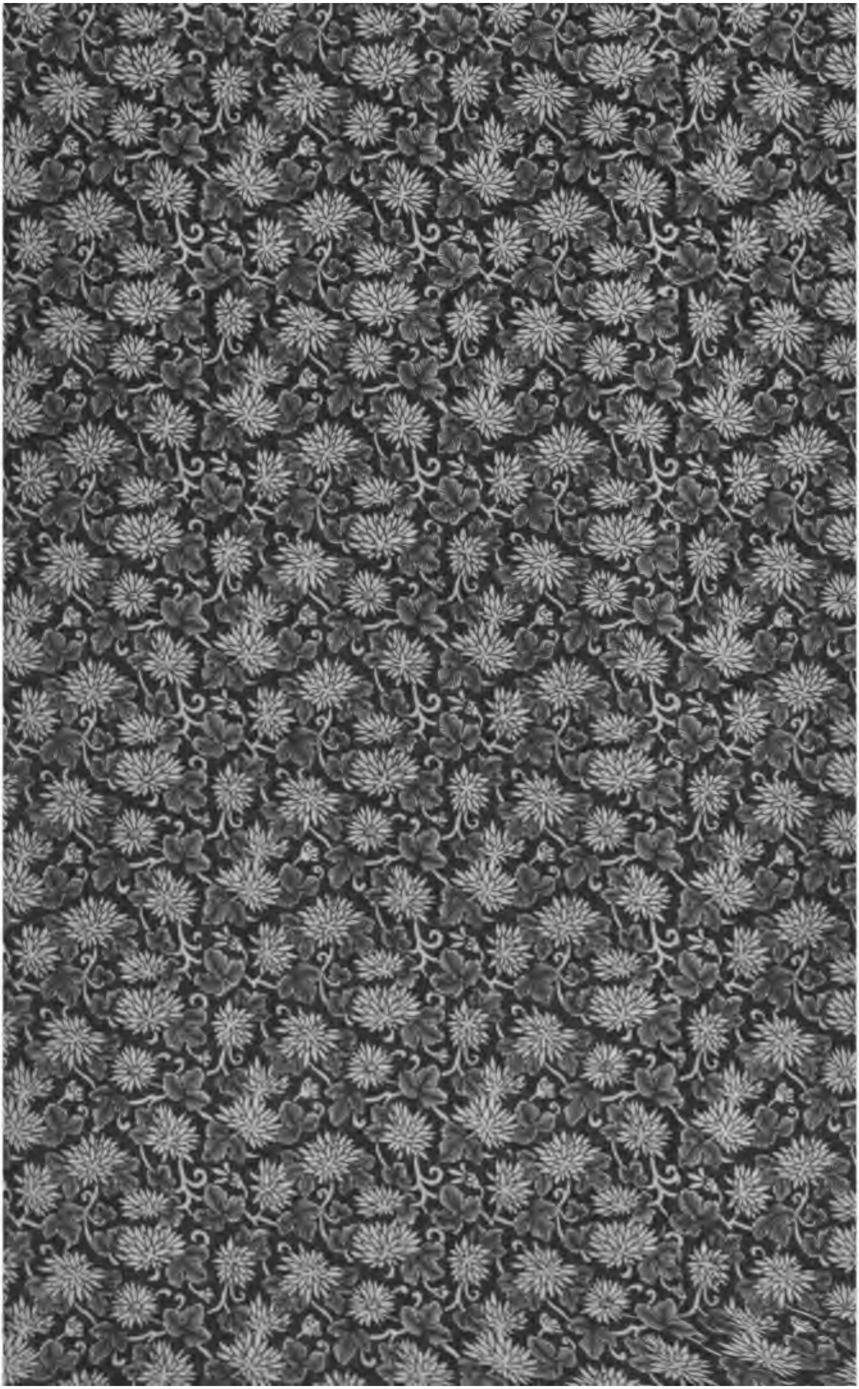
Google's mission is to organize the world's information and to make it universally accessible and useful. Google Book Search helps readers discover the world's books while helping authors and publishers reach new audiences. You can search through the full text of this book on the web at `http://books.google.com/`

BUHR A
a39015 01802977 0b

Analysis
Detection and Commercial Value
# of the
Rare Metals

J. OHLY, Ph.D.

1837
ARTES VERITAS SCIENTIA
LIBRARY OF THE
UNIVERSITY OF MICHIGAN
E PLURIBUS UNUM
TUEBOR
SI QUAERIS PENINSULAM AMOENAM
CIRCUMSPICE



SCIENCE LIBRARY
QD
171
.037
1907

31

Analysis,
Detection and Commercial Value
# of the
Rare Metals.

A treatise on the occurrence and distribution of the
Rare Metals and Earths, the methods of deter-
mination and their commercial value
in the arts and industries with
a historical and statisti-
cal review of each.

BY

J. OHLY, Ph.D.

Third Edition.

1907
THE MINING REPORTER PUBLISHING COMPANY
DENVER, COLORADO, U. S. A.

COPYRIGHT 1907
BY
THE MINING REPORTER PUBLISHING CO.

Preface

This book has been written according to the principles of modern science, and its contents are expected to find appreciation among practical assayers, chemists and prospectors. The general plan followed has been to arrange the matter treated under six heads, namely:

1. History.
2. Chemistry and Commercial Points.
3. Mineralogy.
4. Detection.
5. Qualitative Determination.
6. Quantitative Estimation.

By pursuing this course the author intended primarily to promote the interest in the study of the rare metals, and secondly to induce renewed research in places not thoroughly investigated at the present time. The writing of the book has been essentially facilitated by reference to several authorities, and the facts of purely scientific interest are but sparingly mentioned. It is, therefore, a work which is of greater interest to the technologist and manufacturer than to the theorist, practical points having been selected in preference, and the directions for the quantitative estimation of the several rare minerals having been limited to the most necessary details. The historical data will be read with interest, as they show the manner in which the difficulties encountered were conquered. As to the mineralogical part of the publication, the places of occurrence of the rare minerals in this country are given more elaborately, while the enumeration of foreign localities is necessarily brief. If, therefore, the present work should assist in promoting the search for the habitat of the rare minerals and the determination of their properties and uses, the exertion and expense incurred will be amply repaid.

In conclusion the author hopes that his work may be the means of helping those for whose benefit he has written, and would solicit the assistance of anyone using the book by pointing out any errors which may have escaped his attention.

DR. J. OHLY.

Contents

Introduction 7
Chapter
I. Tungsten 9
II. Niobium 19
III. Thallium 28
IV. Tantalum 37
V. Molybdenum 46
VI. Tellurium 57
VII. Platinum and the Platinum Metals 68
VIII. Palladium 80
IX. Rhodium 85
X. Osmium 89
XI. Ruthenium 93
XII. Iridium 98
XIII. Selenium 103
XIV. Germanium 109
XV. Uranium 115
XVI. Indium 128
XVII. Gallium 133
XVIII. Vanadium 138
XIX. Beryllium 154
XX. Thorium 162
XXI. Zirconium 173
XXII. Cerium 187
XXIII. Lanthanum 202
XXIV. Ytterbium 204
XXV. Scandium 206
XXVI. Titanium 209
XXVII. Lithium 222
XXVIII. Caesium 235
XXIX. Rubidium 238

Appendix 241
Analysis of Vanadium and Uranium Ores........ 241
Separation of Iron from Uranium........ 245
Analysis of Vanadinite........ 246
A Rapid Process........ 246
Estimation of Molybdic Acid........ 247
Separation of Tungsten and Molybdenum........ 247
Detection of Ni, Co, Mn and Zn........ 248
Detection of both Cobalt and Nickel........ 249
Test for Cobalt........ 249
Quantitative Separation of Nickel and Cobalt from Zinc and Manganese........ 250
Quantitative Estimation of Chromium........ 253
Volumetric Estimation of Antimony........ 254
Volumetric Method for Determining Magnesia........ 255
Separation and Estimation of Potassium and Sodium in Rocks 256
Estimation of Sulphur in Coal........ 258
Electric Furnace 259
Chemical Analysis of Crude Petroleum and Oil Rock... 259
Radium 273
Molybdenite and the Commercial Products Therefrom.. 278
Analytical Methods 288
Volumetric Determination of Uranium........ 288
Determination of Molybdenum by Mercurous Nitrate.. 288
Determination of Tungsten by Mercurous Nitrate..... 289
Determination of Vanadium........ 289
Determination of Molybdenum as Barium Molybdate... 290

Introduction

The elements usually distinguished as the "rare" metals are steadily growing in importance, and it is more than likely that they will lose their epithet of "rare" in proportion as efforts are made to ascertain their habitat and to establish their peculiarities.

The table given shows the analytical classification of the rare metals according to their behavior toward the qualitative group reagents, and is to be regarded as the basis underlying the course of investigation pursued. It will be noticed that none of the rare metals occur in the fourth group, which circumstance finds explanation by the fact that none of them approaches the behavior and characteristics of the three members barium, strontium and calcium sufficiently to justify their classification with the latter.

When considering past experiences in the location of deposits containing rare metals, the observer is forcibly impressed with the fact that an urgent demand for any of them has never failed to cause strenuous efforts being made in prospecting for them, and that in every case the final results have been most gratifying. Demands of this kind originate, however, from a close study of the respective elements and their compounds, followed by their adaptation to certain manufactures, when, as a natural consequence, circumstances arise, which incite to renewed efforts and finally bring the pecuniary benefit desired. In connection with this train of thought the deplorable fact presents itself that through the prevailing tendency at American universities and colleges of considering inorganic chemistry as a closed book, and of concentrating efforts mainly upon the imitative study of the carbon compounds and the ludicrous "chasing of the atoms," immeasurable harm has been done to the progress of our knowledge of the rare metals, any important discovery of that character having reached us from abroad, that is from England, Germany, France, Sweden and Russia. Our limited knowledge of the application of some of the rare metals, as niobium and tantalum, in manufactures, is therefore partly attributable to the indifference shown in this regard by the higher schools of learning, to which the prospectors and practical miners naturally look for guidance. Mainly for this reason the commercial application of niobium and its compounds, like that of several other rare metals, has not found the attention it deserves, due allowance being made for the scarcity of the minerals carrying it—which point, however, must remain an open question as long as the fundamental researches leading to practical success are neglected.

CHAPTER I.

TUNGSTEN (Wolfram).

CHEMISTRY AND COMMERCIAL POINTS.—Atomic weight 183.6 (Roscoe). The high grade quality of tungsten ore ranges in contents of tungstic acid (WO_3), from sixty to seventy per cent., and the average selling price for such ores was $160 per ton in 1900. The production of metallic tungsten, ferro-tungsten, tungsten trioxide and sodium tungstate amounted to seventy-six tons; the metal brings from 82 cents to $1 per pound, and ferro-tungsten from 30 to 35 cents per pound. The states of Colorado, Arizona, Nevada, South Dakota and Connecticut contributed by shipments to the annual production; deposits of tungsten ore were discovered in Montana, New Mexico, Idaho, Oregon, Washington, California and North Carolina. A few years ago all the tungsten employed in the United States was imported from European countries; subsequent prospecting, however, elicited the fact that the mineral was present in large quantities at home, thus showing that its classification with the ''rare'' metals is decidedly on the decline.

Though metallic tungsten has a high melting point, it is readily taken up by steel, and forms then a hard, compact alloy, which is employed for the manufacture of self-hardening tools, which are not impaired by heat, and as a consequence may be driven much faster than carbon steel, when used as machine cutting tools. Ferro-tungsten assimilates yet more readily with molten steel, and the finished product serves for the preparation of mechanics' tools and other instruments of great hardness. A very distinctive characteristic of tungsten steel is its capability of taking a higher degree of magnetization than any other steel, while it resists atmospheric corrosion, damascenes finely, and withstands the effects of sea water to a remarkable degree. It has been found that the most advantageous time of adding the tungsten to the steel is during the latter stages of the manufacture, and that a tungsten steel containing five to six per cent. of the metal is very hard and tenacious, though workable, and that an incorporation of ten to twelve per cent. tungsten renders the alloy so hard that it cannot be worked with the lathe, and must, therefore, be forged or ground.

The metal is readily obtained in pure condition by the reduction of the trioxide WO_3, with a calculated amount of charcoal in the electric or regenerative gas furnace. For this purpose the oxide is mixed with eleven to twelve per cent. charcoal and five per cent. pitch or rosin, when tungsten separates out under the effect of the furnace heat in the form of a dense white metal. In order to produce ferro-tungsten, the crushed tungsten ore is incorporated with a calculated amount of iron oxide or scrap, when a mixture of ten to twelve per cent. pulverized quartz is added, to which five per cent. of pitch or rosin is given, in case the ore is very rich, and the mass placed in crucibles and smelted in a specially constructed furnace. The product obtained in this manner is a ferro-tungsten of fine quality, which settles in the bottom of the crucibles in the form of a metallic ingot.

A good commercial ferro-tungsten should have an average composition approaching the following figures.

Tungsten	78.80	per cent.
Iron	15.90	per cent.
Carbon	3.20	per cent.
Silicon	1.87	per cent.
Sulphur	0.11	per cent.
Phosphorus	0.10	per cent.
	99.98	per cent.

It should be free of arsenic and other impurities.

In the manufacture of the trioxide, sodium tungstate is first made by mixing the tungsten ore with soda in proper proportion to form that salt, and the mixture is then roasted in a reverberatory furnace, so that the mass sinters. The product thus obtained is withdrawn while hot, and thrown in a vessel holding a little water, so as to disintegrate the mass. In this manner the insoluble residue of iron, lime and tin, which latter is frequently present in small amounts as cassiterite, SnO_2, is removed, and the solution further purified, after addition of more water, by evaporation. The concentrated heated liquid is then treated with hot hydrochloric acid, when the trioxide WO_3, separates out in form of a yellow powder, which is recovered by filtering and washing.

The commercial applications of tungstates, like the normal salt, $Na_2WO_4+2H_2O$, and the so-called meta tungstate of sodium, $Na_2W_4O_{13}+10H_2O$, are numerous. The former, when used in solution for the saturation of materials, prevent these substances from bursting into a flame and allow them only to smoulder away slowly. The reduction of the potassium tungstates by fusion with tin gives rise to peculiar compounds, which have various colors, possess metallic lustre, and are applied as tungsten bronzes. The polytungstates are employed most advantageously for this purpose, and after their fusion with tin, are first treated with caustic soda and then with hydrochloric acid. The same salts, when subjected to the effect of the electric current, give deep-blue coppery crystals, whose composition is $K_2WO_4 4H_2O$. The so-called "Magenta bronze" results when tungsten trioxide is added to fused potassium as long as it dissolves, when the whole is gently heated in a current of hydrogen, and digested successively with water, hydrochloric acid, potash and water, leaving small violet crystals of copper lustre of the composition $K_2W_4O_{12}$. Finally "Saffron bronze," $Na_2W_3O_9$, is prepared like the potassium salt. It forms beautiful, golden, cubic crystals, unattacked by alkalies or acids, except hydrofluoric acid. A mixture of the potassium and sodium bronzes is used for the production of a violet pigmet.

Sodium tungstate is also employed in place of sodium stannate as a mordant in dyeing and painting, especially for wool and silk, and also for decolorizing acetic acid and acetates prepared from pyroligneous acid. The compound is also used as a decorticator in preparing raw fibers for manufacturing. Other tungstates, like lead tungstate, prepared by the precipitation of sodium tungstate with lead acetate, and those of zinc and barium, especially the latter, are used as a substitute for white lead.

The pure trioxide is a fine bright canary yellow powder, which acquires, on exposure to light, a greenish tint. It is used as an oil and water color, and is quite permanent. When heated to 250° C. in a current of hydrogen, the trioxide is reduced to a blue oxide, $2WO_3WO_2$, and this compound also finds application as a pigment.

Metallic tungsten in powder form is a commercial article and contains usually from ninety-five to ninety-eight per cent. of the metal. Furthermore a tungsten-nickel alloy carrying seventy-five per cent. of the metal and five per cent nickel occurs in the market, and analyzes as follows:

Tungsten, about	74 per cent.
Nickel, about	24 per cent.
Iron, from	2.00 to 2.50 per cent.
Carbon, from	0.75 to 1.00 per cent.
Silicon, from	0.25 to 0.50 per cent.

This is a very remarkable and interesting alloy, and is of special advantage in case nickel is required together with tungsten. When alloyed with nickel, the tungsten can be introduced into the steel with great accuracy, and very reliable results be obtained by means of it.

An alloy of aluminum and tungsten, known as partinium, and manufactured by Henry Partin of Puteaux, near Paris, is (now) largely used in automobile construction. Most vehicles at the last Paris show had partinium bodies. The alloy is very light and strong. It is manufactured in profiled sections and sheets as well as castings.

History and Mineralogy.

In former years the mineral "tungsten," which means in Swedish "heavy stone," was erroneously taken for tin ore, until the mistake was cleared by Cronsted. Scheele, the illustrious Swedish chemist, showed in 1781 that the mineral scheelite, thus called after him, contained lime as a base and a peculiar acid, which was recognized in the same year by Bergmann as a metallic compound.

The three tungsten minerals of commercial importance are wolframite, huebnerite and scheelite, of which the first named has a hardness of 5 to 5.5, and a specific gravity of 7 to 7.5. It is a tungstate of iron and manganese, represented by the formula $FeOMnOWO_3$, so that it may be considered as an isomorphous mixture of $FeWO_4$ and $MnWO_4$. Its appearance is black to brownish black, its lustre resinous, metallic or adamantine, and it has a streak verging between black and reddish brown, according to the prevailing proportion of iron or manganese. When in pure condition its composition is represented as follows:

Tungsten trioxide WO_3	76 per cent.
Ferrous oxide FeO	9.5 to 20 per cent.
Manganous oxide MnO	4 to 15 per cent.
Niobic acid Nb_2O_5 in cases	1.1 per cent.

It is known to occur in commercial quantities in Boulder county, Colorado, and at Red Mountain, Ouray county, Colorado. The ore of Boulder county concentrates to sixty-five per cent, tungsten trioxide, and that of San Juan county to seventy-three or sixty-eight per cent. Several tons of wolframite were also mined and shipped from Sunday gulch, near Oreville, Pennington county, South Dakota, and from the Harrison mine at Lead, South Dakota.

Huebnerite, which was named from Dr. Huebner, a prominent German chemist and mineralogist, who first analyzed it, is second in importance and occurrence. It has a hardness of 4.5, and a specific gravity of 7.14, possesses a perfect cleavage, and occurs usually in bladed forms, rarely in distinct crystals. Its color varies from brownish red to hair brown and nearly black, while its streak verges from yellowish brown to greenish gray. Its composition is given by the figures:

WO_3	76.9 per cent.
MnO	23.1 per cent.

so that it is to be considered as a manganese tungstate, $MnWO_4$, when pure, the percentage of tungstic acid being nearly constant in all varieties. The ore occurs in commercial quantities in San Juan county, Colorado, the Dragoon mountains, Cochise county, Arizona, and at Osceola, Nevada, the latter averaging in part seventy-five per cent. in tungstic acid.

The third and next important tungsten ore, known as scheelite, has a hardness of 4 to 4.5 with a specific gravity of 5.9 to 6.2, and a tolerably perfect celavage. Its color varies from colorless to yellow or brown, and its streak is white. The gray, yellowish, clove-brown or reddish variety is the most frequent, especially in Colorado. Its composition in a state of purity is represented as follows:

WO_3	80.55 per cent.
CaO (calcium oxide)	19.45 per cent.
	100.00 per cent.

Commercial quantities are found near Long Hill, Trumbull township, Connecticut, together with wolframite, and the percentage of tungsten trioxide amounted after concentration to sixty-seven and seventy per cent, for scheelite, and to fifty-five and sixty per cent. for wolframite. Limited deposits of scheelite have been discovered in the San Juan district, Colorado.

DETECTION.—The presence of tungsten is readily ascertained by boiling the finely powdered mineral with a mixture of four parts hydrochloric acid and one part nitric acid for about two hours in a porcelain dish, when, in case the ore contains tungsten, yellow spots of tungsten trioxide will be discernible. The trioxide is insoluble in dilute hydrochloric acid.

If heated in the oxidizing flame of the blowpipe with borax or phosphorous salt, all tungsten compounds form colorless beads.

In the reducing flame they produce with borax a yellow glass, in case the quantity of tungsten is large. Small amounts added to the bead leave it colorless. When heated with phosphorous salt in the reducing flame, a glass of pure blue color is produced, as long as tungsten compounds are present exclusively. On adding a particle of iron salt to the bead, it assumes a blood-red coloration, and on introducing tin, the bead becomes blue or bluish-green.

CHEMICAL REACTIONS.—The trioxide is almost insoluble in a large excess of hydrochloric or nitric acids, which circumstance distinguishes it from molybdenum trioxide, MoO_3, but it dissolves readily in ammonia.

H_2S produces no precipitate in acid solutions of tungstates, but reduces the WO_3 to the blue oxide W_2O_5.

$(NH_4)_2S$ produces no precipitate from alkaline tungstates, but on acidulating with HCl, light brown tungsten trisulphide WS_3 is precipitated, slightly soluble in pure water, but insoluble in the presence of salts. The solution is colored blue. The precipitated sulphide dissolves readily in ammonium sulphide.

$SnCl_2$ gives at first a yellow precipitate; on acidulating with HCl and applying heat, the precipitate acquires a beautiful blue color. This reaction is very delicate and highly characteristic.

Zinc subsulphite, obtained by treating a sulphite with zinc, reduces tungsten compounds to a deep brown tungstous oxide of unknown composition; in small quantities a deep blue color only may be produced.

QUANTITATIVE DETERMINATION.—Reduce the ore to a very fine powder, weigh off one gram, and digest for twelve hours (over night) at a gentle heat with a mixture of four parts hydrochloric and one part nitric acid, till yellow pulverulent tungstic acid remains. Evaporate to dryness on water-bath, and take up with water acidulated by hydrochloric acid. Filter, wash the residue, consisting, besides the yellow trioxide, of silica and sometimes small quantities of niobic acid, with alcohol, and treat the mixture on the filter with ammonia. Place the filtrate in a large weighed porcelain crucible, evaporate to dryness on the water-bath, and heat the residue of ammonium tungstate to decomposition. Weigh the crucible with the remaining trioxide, and calculate the percentage. This method is due to Woehler.

In a separate part of two grams of the ore, placed on a large watchglass, determine the water contents by heating in an air-bath to 110° C. for a couple of hours, and weigh. Calculate the moisture contained in the ore from the loss in weight.

CHAPTER II.

NIOBIUM.

HISTORY.—The historical facts pertaining to the discovery of niobium are of a rather peculiar and interesting nature. In 1801 a specimen of a black mineral, found at Naumeag, Connecticut, and sent by Governor Winthrop of that state to Sir Hans Sloane, then president of the Royal Society, London, was submitted to the English chemist, Charles Hatchett, for examination and analysis. Having finished his researches, he declared to have established the presence of a new metal in the mineral which he aptly named columbium. Subsequently he published his observations and the results of his analytical work in the Philosophical Transactions of 1802. Seven years later the English chemist Wollaston took up the investigations of Hatchett, and pronounced the metal to be identical with tantalum, which had been discovered in 1802 by Ekeberg, a Swedish scientist. This conception was generally upheld until 1846, when the German chemist, Rose, after carefully investigating the properties of the metal and its compounds, renamed it, calling it "niobium," from Niobe, the daughter of Tantalus, known in Greek mythology as having provoked the hatred of Apollo and Diana by her excessive pride in her children, who were slain by the gods, while she herself was changed into stone. This appellation "niobium" has been accepted ever since Rose made the results of his investigations known, though it is claimed by some that the name "columbium" should be maintained in deference to its discoverer, Hatchett.

CHEMISTRY AND COMMERCIAL POINTS.—The metal niobium, atomic weight 94.2 and specific gravity 7.06, has been isolated and may be bought at the works in Germany or indirectly from Messrs, Eimer & Amend, New York, at the price of $4 per gram or 15.432 grains. It is a steel-gray metal of fine lustre, which burns when gently heated in air to form the pent-oxide, Nb_2O_5, and is not attacked at ordinary temperatures by hydrochloric or nitric acid, nor by a mixture of the two, but dissolves readily in concentrated sulphuric acid, forming a colorless solution. It may be justly called a rare metal, since it is known, so far, to occur in nature in but few minerals of limited occurrence. This circumstance does not exclude the possibility, however, that on closer study of its properties, and more intimate research concerning its characteristics, the mineral compounds of the element may be traced further and their habitat established more extensively. Niobium is found most frequently in combination with tantalum, and is then present in the natural products as the pentoxide in association with the corresponding tantalum compound, Ta_2O_5, both being combined with metallic bases so as to form niobates and tantalates. Chemical formula, Nb. The element niobium has no commercial application, nor is there any record of the salts of niobium being used in the arts.

MINERALOGY.—The mineral columbite being one of the most interesting of the niobium ores, and its occurrence in commercial quantities being known, it deserves first consideration. It is found in the Pike's Peak region, together with microline, an aluminum potassium sodium silicate, resembling orthoclase felspar, and at Turkey Creek, Jefferson county, Colorado; also in the Black Hills district, South Dakota, where it occurs in granite veins, associated with cassiterite, beryl and spodumene. In the latter locality the mineral appears in crystals and crystalline groups, frequently of large dimensions, a mass weighing two thousand pounds having been located. The Etta and Bob Ingersoll mines in Pennington county are, however, the most prolific producers of columbite, while the mineral occurs in smaller quantities in the Nigger Hill district, Lawrence county, and is there frequently found in association with stream tin. The eastern and southern states, like Maine, New Hampshire, Massachusetts, Connecticut, Pennsylvania, New York, Virginia and North Carolina, possess also deposits of columbite, some of the specimens found near Haddam and Branchville, Connecticut, weighing many pounds.

The prevailing color of columbite is iron-black, though varieties occur which vary from grayish to brownish black, all three being opaque. Besides these a rare columbite of reddish-brown color is met with which is translucent. Many of these minerals exhibit a sub-metallic brilliant lustre and a beautiful irridescence, and all of them show a streak verging from dark red to black. They are brittle, of uneven fracture, of rather distinct cleavage, hardness of about 6, and have a specific gravity lying between 5.3 and 7.3. A columbite from Turkey Creek, Colorado, showed a specific gravity of 5.383, and had the following composition:

Nb_2O_5	73.45	per cent.
Ta_2O_5	2.74	per cent.
SnO_2	1.35	per cent.
WO_3	1.14	per cent.
FeO	11.32	per cent.
MnO	9.70	per cent.
CaO	0.61	per cent.
Total	100.31	per cent.

The several varieties taken from the Etta mine gave analytical percentages varying between the following figures:

Nb_2O_5	54.09	29.78
Ta_2O_5	28.20	53.28
SnO_2	0.10	0.13
FeO	11.21	6.11
MnO	7.07	10.40
CaO	0.21	None
	100.88	99.70

The specific gravity of the mineral highest in niobium percentages was 5.89, and that of the lowest 6.75.

Another niobium ore, known as pyrochlore, which is found in Norway and is said to occur also in the syenite of St. Peter's Dome, Pike's Peak, Colorado, consists essentially of a niobate and titanate combined. It usually crystallizes in octahedra, is met with sometimes in irregular grains, has an octahedra cleavage, conchoidal fracture, is brittle, and possesses a hardness of 5 to 5.5, and a specific gravity varying between 4.2 and 4.36. Its color verges from dark red to brown and blackish brown, and it shows a streak lying between light brown and yellowish brown, while its lustre is vitreous, but resinous on fractured surfaces. It is slightly translucent or opaque. Its composition is shown by the following analytical data:

Nb_2O_5	58.27 per cent.
TiO_2	5.38 per cent.
ThO_2	4.96 per cent.
Ce_2O_3	5.50 per cent.
CaO	10.93 per cent.
FeO and UO	5.53 per cent.
Na_2O	5.31 per cent.
F.	3.75 per cent.
Ignition gave	1.53 per cent.
	101.16 per cent.

Specific gravity. 4.22.

A third niobium ore, known as Hatchettolite, and thus named from the discoverer Hatchett, is chiefly a tantaloniobate of uranium, resembling pyrochlore somewhat in composition, and occurs in the mica mines of Mitchell county, North Carolina. Its form of crystallization is octahedral, its fracture subconchoidal, its hardness 5, and its specific gravity 4.77 to 4.90. It is translucent, brittle, and of resinous luster, while its color is yellowish brown. The following shows its composition:

Nb_2O_5 and Ta_2O_5	66.01	per cent.
WO_3 and SnO_2	0.75	per cent.
UO_3	15.20	per cent.
CaO	7.72	per cent.
Y_2O_3	2.00	per cent.
FeO	2.08	per cent.
K_2O	0.50	per cent.
H_2O	5.16	per cent.
	99.42	

Fergusonite is another niobium mineral, consisting mainly of a niobate and tantalate of yttrium, and deserves mention on account of its large contents in niobium pentoxide. It occurs at Rockfort, Massachusetts, in granite, with zircon near Storeville, Anderson county, South Carolina, and in association with magnetic and other minerals in large rough crystals at the gadolinite locality in Llano county, Texas, five miles south of Bluffton, on the west bank of the Colorado river. It is brittle, translucent to opaque, has a brownish-black color and appears light liver-brown when split in thin leaves. It gives a pale brown streak, imperfect cleavage, subconchoidal fracture, and has a hardness varying between 5.5 and 6, while its specific gravity is usually 5.8, which figure is lowered in cases to 4.3 by hydration. Its external lustre is dull, but on fractured surfaces brilliantly vitreous and submetallic. A specimen from Llano, Texas, had the following composition:

Nb_2O_5	42.79
UO_2	3.93
UO_3	3.12
ThO_2	0.83
Y_2O_3 and Er_2O_3	31.36
FeO	3.75
CaO	2.74
H_2O	8.19
F	0.50
Al_2O_3	0.85
PbO	1.94
	100.00

DETECTION.—Since the oxides of niobium are perfectly insoluble in acids after ignition, a ready means is given thereby for their detection, the only compounds which share this property with them being those of tantalum. Furthermore, the niobium oxides remain behind in an insoluble condition after being fused with an excess of acid potassium sulphate, and subsequent lixiviation with water. They are distinguished from silica by their behavior before the blowpipe, inasmuch as niobic oxides, when heated in the reducing or inner flame, assume a greenish-yellow color when hot, but become colorless on cooling. When treated before the blowpipe with microcosmic (phosphorus) salt, the bead dissolves large quantities of the oxide, and remains colorless in the oxidizing flame, but becomes violet in the reducing flame, or beautifully blue in case the bead is saturated with the oxide. This color disappears again in the oxidizing flame. On adding ferrous sulphate the bead assumes a blood red coloration. For the reason that all the niobium minerals, discovered so far, are salts of niobic acid, associated with tantalates, which latter resemble the niobates closely, a reliable method for distinguishing the two compounds is of essential importance. This is found in the behavior of the solutions of alkaline niobates and tantalates toward an excess of hydrochloric acid at ordinary temperatures, when the precipitated niobic oxide separates out as a white precipitate insoluble in the liquid, while the precipitated tantalic oxide dissolves and forms a slightly opaline solution.

QUALITATIVE DETERMINATION.—Mineral acids, especially sulphuric acid, even at the ordinary temperatures, precipitate niobic hydrate, nearly insoluble in the acid. (The precipitation of tantalic hydrate requires the aid of heat.)

$(NH_4)_2S$ or NH_4OH precipitates from acidified solutions of Nb_2O_5 the hydrate, containing ammonia, soluble in hydrofluoric acid.

NH_4Cl precipitates the acid, but only slowly and incompletely, more especially if in the presence of alkaline carbonates.

K_4FeCy_6 gives, with a solution of an alkaline niobate, which has been acidulated with sulphuric or hydrochloric acid, a red precipitate.

$K_6Fe_2Cy_{12}$ gives a bright yellow precipitate.

Infusion of galls produces an orange-red precipitate.

A piece of zinc immersed in an acidulated solution, forms a beautiful blue precipitate, which after a time changes to brown. (Tantalates yield none or only a faint blue color.)

QUANTITATIVE ESTIMATION.—Fuse one gram of the finely pulverized niobium mineral (columbite) in a platinum crucible with six or eight times its weight of acid potassium sulphate; pulverize the cooled mass and boil it repeatedly with fresh quantities of distilled water, till all the potassium, iron or manganese sulphates formed have entered in solution. Filter and digest the residue, consisting of hydrated niobic acid, ferric oxide, stannic and tungstic acids, in ammonium sulphide, containing an excess of sulphur, in order to dissolve the stannic and tungstic acids, and to change the iron into the sulphide. Filter, wash the impure niobic acid with water containing ammonium sulphide, boil with concentrated hydrochloric acid to remove the remaining iron, manganese, uranium, cerium, copper and other metallic compounds, filter and finally wash the residue with boiling water. Dry, ignite, so as to change the hydrated niobic acid into the anhydride Nb_2O_5, and weigh.

CHAPTER III.

THALLIUM.

HISTORY.—Thallium was discovered in 1861 by Sir William Crookes in a seleniferous deposit obtained from the lead chambers of the sulphuric acid works at Tilkerode in the Hartz mountains, Germany, where iron pyrites are employed for the production of the acid. Deposits of this kind were known to contain selenium, but when the mass had been treated for the recovery of that metal, a considerable residue remained, which was first supposed to consist of tellurium compounds. On testing this residue by spectral analysis, the discoverer observed, however, a single sharp and brilliant green line, characteristic of the metal and its compounds, which circumstance led subsequently to its appellation, since metallic thallium was found to burn with a beautiful green flame, when heated in the air. It was hence named by Crookes "thallium," a term derived from the Greek noun, signifying a green shoot or bud.

Toward the end of the year 1861 the discoverer obtained thallium in distinct metallic form, and soon afterwards M. Lamy, who made his researches independently from and almost simultaneously with Crookes, exhibited magnificent specimens of the metal.

cast in solid bars, at the last great exhibition in London.

Chemistry and Commercial Points.—Thallium of the atomic weight 204.1, specific gravity 11.8, and fusing point 290° C., is a tin-white, crystalline, malleable metal, which may be acquired in quantities of ten grams from the same sources mentioned under niobium, at $1.50, or 15 cents per gram. It has a low degree of tenacity, being as soft as sodium, and resembles lead in possessing nearly the same atomic weight and specific gravity. (Lead, at, wt. 206.91; sp. gty. 11.4; fusing point 325° C.) Like graphite it marks paper readily, producing a streak, which is blue at first, turns gradually yellow and fades away in a day or two. On account of its softness it may be cut with a knife or even scratched with the fingernail. When heated in the air it volatilizes at a red heat, forming brown vapors of oxide, and boils at a white heat. It may be distilled in a current of hydrogen, thus excluding the oxidizing effect of atmospheric oxygen. Metallic thallium does not decompose water at ordinary temperatures, but acquires that capacity when heated to redness. It oxidizes rapidly in moist air or under aerated water, producing thallous hydrate of the formula $TlOH$. The latter, as well as the carbonate and silicate, are soluble to some extent in water, while the readily soluble sulphate unites with aluminum sulphate to produce a true alum, like the corresponding salts of potassium, sodium and ammonium. On the other hand thallous chloride, $TlCl$, combines with platinic chloride to form a double salt insoluble in water. The metal dissolves readily in sulphuric and nitric acids, but is only slightly affected by hydrochloric acid, owing to the insolubility of thallous chloride. Thallium salts are extremely poisonous, producing symptoms like those observed in cases of lead poisoning. The metal or its compounds find industrial application in the manufacture of thallium glass, which possesses a higher refractory power than lead glass, and is therefore used for optical purposes and the preparation of artificial stones.

The preparation of metallic thallium from flue-dust deposits of sulphuric acid factories, using pyrites for the production of the acid, comprises, according to the directions given by Crookes, the mixing of the dust in wooden vats with an equal weight of boiling water, and a thorough stirring of the mass, when a considerable quantity of nitrogen dioxide (due to the employment of nitric acid in the preparation of sulphuric acid) is evolved. The mixture is allowed to stand for twenty-four hours, so as to let the undissolved residue settle in the bottom of the vats. The supernatant liquid is then siphoned off, and the residue washed, to be afterwards treated with a fresh quantity of boiling water. The collected liquids siphoned from the sediment, are allowed to cool, and treated with a considerable excess of concentrated hydrochloric acid, whereby an impure thallium chloride is precipitated, which subsides after standing. The salt obtained in this manner is then thoroughly washed on a calico filter, and afterwards squeezed dry. Three tons of the dust yield sixty-eight pounds of this rough chloride, which is further purified by adding small portions of it at a time to half its weight of hot sulphuric acid, placed in a porcelain vessel, the mixture being constantly stirred, and the heating continued until the whole of the hydrochloric acid and the greater portion of the excess of sulphuric acid are driven off. The fused acid sulphate is then dissolved in an excess of water, and an abundant current of hydrogen sulphide passed through the solution, to precipitate arsenic, antimony, bismuth, lead, mercury and silver, eventually present. The sulphides of these metals are separated from the liquid by filtration and the filtrate is boiled until all free sulphuric acid is removed, when it is rendered alkaline by the addition of ammonia, and heated to boiling. The precipitate of iron oxides and alumina, usually appearing at this stage of the process, is removed by filtering, and the clear solution evaporated to a small bulk. Sulphate of thallium then separates out on cooling in long striated crystals, resembling potassium sulphocyanate, the ammonium sulphate present being much more soluble in water than the thallium salt, and hence remaining in solution.

The metal is obtained from the solution of the sulphate either by electrolysis or by the action of zinc. In the first case an electric current from two to three cells, having platinum terminals, is passed through an acidulated solution of thallium sulphate in its own weight of water, when the metal is deposited on the negative pole in brilliant plates and long needle-shaped crystals, stretching out toward the positive pole, and presenting an appearance like that known as the tin tree. The reduction is complete when hydrogen begins to escape at the negative pole. The crystalline metallic sponge may then be squeezed into a compact mass round the platinum terminal, well washed with water, removed from the platinum and kneaded by the fingers into a solid lump.

For reducing considerable quantities of thallium it is best to employ metallic zinc. Plates of pure zinc, which should leave no residue whatever when dissolved in sulphuric acid, are arranged vertically round the sides of a deep porcelain dish holding a gallon. Crystallized sulphate of thallium, in quantities of about seven pounds at a time, is then placed in the dish, and water poured over to cover the salt. Heat is applied and in the course of a few hours the whole of the thallium will be reduced to the state of a metallic sponge, which readily separates from the plates of zinc on slight agitation. The liquid is poured off, the zinc removed and the spongy thallium washed several times. It is then strongly compressed between the fingers and preserved under water, until it is ready for fusion. In this manner upwards of a hundred weight of metallic thallium may be reduced in the course of twenty-four hours.

MINERALOGY.—Crookesite, thus named from the eminent English chemist and physicist Crookes, is a selenide of copper and thallium, but is not known to occur in this country, its habitat being Sweden. Specimens of the mineral show no crystallization, are massive and compact, of hardness 2.5 to 3, specific gravity, 6.90, and have a metallic lustre and a lead gray color. The strongly green coloration of the flame, produced by crookesite, when heated before the blowpipe, is a decisive characteristic of the mineral as well as of all other thallium compounds. Its composition is as follows:

Selenium (Se)	32.27
Thallium (Tl)	18.55
Copper (Cu)	46.11
Silver (Ag)	1.44
Ferrous oxide (FeO)	0.63
	99.00

This mineral is the only one, known so far, which may be considered as a real thallium ore.

The element is, however, disseminated in small quantities through many ores, not considering its presence in certain mineral waters. Thus it occurs in limited amounts in sylvite, KCl; in carnallite, $MgCl_2$, $KCl+6H_2O$, at Strassfurt, Germany, and also in some varieties of iron, copper, zinc and cadmium sulphides, in which it is present in combination with sulphur. Furthermore it is sometimes found in mica and lepidolite, and in calamine, metallic zinc and cadmium, in bismuth, mercury and antimony ores, in selenides and tellurides, and in crude or native sulphur.

DETECTION.—When thallium compounds are treated on charcoal before the blowpipe, they vaporize, and impart an intense green color to the flame. Hydrogen sulphide produces no precipitate in acid solutions of thallous sulphate or nitrate, and throws down only a part of the thallium from neutral solutions of this kind. Thallous solutions, obtained by means of acetic or carbonic acid are, however, differently affected by this reagent, since all the thallium present is precipitated under these conditions in the form of the deep brown sulphide. Hydrochloric acid precipitates from such solutions the difficultly soluble white chlorite, resembling the corresponding silver salt, while potassium iodide throws down an insoluble yellow amorphous thallium iodide.

Thallic salts are readily distinguished from thallous salts by their behavior with caustic and carbonated alkalies, which precipitate brown gelatinous thallic hydrate, TlO OH, insoluble in excess, and furthermore by their deportment toward hydrochloric acid, with which they produce no precipitate.

QUALITATIVE DETERMINATION.—Hydrogen sulphide does not precipitate strongly acidified thallous solutions unless arsenic trioxide, As_2O_3, be present, when a part of the thallium is carried down with the arsenious sulphide formed as a brownish-red precipitate.

Ammonium sulphide precipitates the whole of the thallium as thallous sulphide, insoluble in ammonia, alkaline sulphides, or potassium cyanide. It is readily soluble, however, in dilute hydrochloric, sulphuric, or nitric acids, but difficultly soluble in acetic acid. When exposed to air, thallous sulphide is rapidly converted into thallous sulphate. On heating it fuses and volatilizes.

Caustic potash, soda, or ammonia does not precipitate aqueous solutions of thallous salts.

Carbonated alkalies produce a precipitate only from concentrated solutions, thallium carbonate (Tl_2Co_3), being soluble in twenty parts of water.

Hydrochloric acid or soluble chlorides and bromides throw down white thallous chloride, $TlCl$, or the bromide, $TlBr$; the precipitate subsides readily, and is unalterable in the air. It is very slightly soluble in boiling water, and still less so in hydrochloric acid.

Potassium iodide precipitates even from the most dilute thallous solutions light yellow thallous iodide, TI, which is almost entirely insoluble in water, but somewhat more soluble in a solution of potassium iodide. This behavior constitutes the most delicate reaction for thallous salts.

Potassium bichromate precipitates thallous chromate, CrO_2TlO_2, insoluble in cold nitric or sulphuric acids.

Platinic chloride precipitates difficultly soluble, pale orange-colored thallous platinic chloride, of the formula $2TlCl.PtCl_4$. Zinc precipitates metallic thallium.

QUANTITATIVE ESTIMATION.—Weigh off five grams of the flue dust and treat them according to the directions given under "chemistry and commercial points," so as to produce a solution of thallium sulphate. Add to the heated liquid an alkaline sulphite solution in order to reduce any thallic salt, eventually present, to the thallous state, and mix a few drops of ammonia with the liquid. Stir and introduce a dilute solution of potassium iodide into the mixture, when the thallium present will be immediately thrown down as a light yellow precipitate of thallous iodide, TlI. Allow to stand for about two hours, collect the precipitate on a weighed filter, wash with dilute alcohol, in which the iodide is insoluble, dry at 115° C., and weigh. The precipitate contains 49.40 per cent. of thallium. Avoid excess of potassium iodide, since thallous iodide is somewhat soluble in a solution of that salt.

CHAPTER IV.

TANTALUM.

History.—Among the historical data referring to the discovery of niobium the name of the Swedish chemist Ekeberg was given, as he was instrumental in establishing the identity of the element tantalum. He discovered the metal when examining two until then (1802) unknown minerals, one of which was found at Kimito, Finland, and the other at Ytterby, Sweden. He named these minerals tantalite and yttrotantalite respectively, and the metal contained in them "tantalum," in allusion to the "tantalizing" difficulties encountered by him in obtaining a solution of the minerals in acids. This circumstance was considered at that time as a very unusual occurrence. When giving this name to the new metal he had reference to the mythical Phrygian king, Tantalus, of Greek mythology, whose daughter Niobe was previously mentioned in connection with the appellation of the metal niobium. According to the conceptions of the ancients, this king underwent in the nether world an excruciating punishment, having provoked the wrath of Jupiter, by being placed up to his chin in a lake, the waters of which receded whenever he tried to partake of them, while alluring fruit, hanging within reach, was lifted by an unseen hand the moment he ventured to grasp it. To increase his anguish, a huge rock was hung suspended above his head and threatened to fall and crush him without warning.

CHEMISTRY AND COMMERCIAL POINTS.—The rare metal tantalum, of atomic weight 182, and specific gravity 10.78, has an iron-gray lustre when burnished, and is a good conductor of electricity. It burns to tantalum pentoxide, Ta_2O_5, when heated long enough in the air to oxidize thoroughly. The metal is insoluble in the mineral acids, including aqua regia, and dissolves slowly in heated hydrofluoric acid. The chemical works in Germany, and Messrs Eimer and Amend of New York, furnish the metal at $9.50 per gram. It is usually prepared by fusing in an iron crucible three parts of sodium fluotantalate of the formula $Na_2TaF_7+H_2O$ with one part of metallic sodium, the mixture being covered with a protective layer of potassium chloride. The ensuing reaction is very violent, and proceeds under the apparition of fire and the development of great heat, after which the mass is allowed to cool. The metal obtained in this manner is of granular form, and is freed from the adhering sodium salts by washing with water.

MINERALOGY.—The mineral tantalite, which deserves first consideration under this caption, is a tantalate of iron and manganese of the generic formula $FeMnTa_2O_6$, and is often accompanied by small percentages of cupric oxide and lime, as becomes apparent from the following analytical data:

Tanatalum pentoxide	84.15
Stannic oxide	0.32
Ferrous oxide	14.68
Manganous oxide	0.90
Lime	0.07
Cupric oxide	1.81
	101.93
Specific gravity	7.197

The habitat of the mineral is Finland, Sweden, France and the United States, the towns of Broddbo and Finbo, near Fahlun, in Sweden, and Chanteloub, near Limoges, in France, being localities where the occurrence of tantalite was first observed. It has since been found, however, in several states of the Union, among them Dakota, Alabama, North Carolina, Connecticut (at Haddam), and in Massachusetts, in which latter state it occurs usually together with columbite. Furthermore the minerals cassiterite, pitchblende and wolframite are known to carry appreciable quantities of the pentoxide in cases.

A tantalite from Cousa county, Alabama, which occurs there in form of peas, disseminated through decomposed granite, analyzed as follows:

Ta_2O_5	79.55
WO_3	1.10
ZnO	0.87
MnO	3.72
FeO	13.51
CaO	0.89
	99.64

Specific gravity ....7.305 to 7.401

The occurrence of tantalum in association with niobium has been mentioned in the chapter treating on that metal.

The color of the mineral tantalite varies from cinnamon brown to black brown and iron black, while its lustre is imperfect—metallic. Specimens are as a rule opaque and have a hardness lying between 6.0 and 6.5, and a specific gravity varying between 7 and 8. The mineral occurs in the crystallized and massive form, sometimes imbedded in granite, when it forms fragments of rounded or irregular shape.

Yttrotantalite, represented, when pure, by the formula $5YO.Ta_2O_5$, and loranskite, a new mineral lately discovered at Imbilax, Finland, are of special interest and importance, since the latter approaches the historical mineral somewhat in composition, while it differs from it by its contents in zirconium. It has been only partially analyzed.

	Yttrotantalite.	Loranskite.
Ta_2O_5	57.27 per cent.	49.00
WO_3	1.85 per cent.	
SnO_2	0.10 per cent.	
Y_2O_3	18.64 per cent.	13.00 (Ce_2O_3 and Y_2O_3)
UO_2	5.10 per cent.	
CaO	4.78 per cent.	
MgO	0.75 per cent.	
FeO	4.82 per cent.	20.00 (ZrO_2)
CuO	0.69 per cent.	
H_2O	6.00 per cent.	
	100.00 per cent.	82.00

Yttrotantalite occurs in varieties verging in color from yellow to brown and black, the first and last being opaque, while the brown mineral is slightly translucent, when split in thin plates. Their hardness varies from 4.5 to 5.5, and their specific gravity from 5.395 to 5 882. The yellow and brown varieties show a white streak, the black, however, a gray one. The yellow mineral possesses a resinous luster on the surface, which becomes vitreous by fracture. On the other hand the luster of the brown variety is vitreous, inclining to resinous, and that of the black mineral submetallic. The several varieties of yttrotantalite are not acted upon by acids, and give off, when heated, appreciable amounts of water (from four to six per cent.); are infusible before the blowpipe, but decrepitate and assume then usually a lighter color. They dissolve in the borax bead.

The new mineral loranskite is described as being brittle, of conchoidal fracture and strong submetallic luster, and as having a hardness of 5 with specific gravity of 4.6. The specimens examined were translucent on the edges, and showed a greenish gray streak.

DETECTION.—In contradistinction to niobium pentoxide, the analagous compound of tantalum does not produce a red bead on the addition of ferrous salt, when heated with microcosmic salt before the blowpipe. Hydrochloric and sulphuric acids precipitate from solutions of alkaline tantalates white tantalic acid, which dissolves in excess of the former, but is insoluble in an excess of the latter. Carbon dioxide, when conducted through the solution of an alkaline tantalate, throws down all the tantalic acid present in the form of an acid salt. Ammonium chloride causes the complete precipitation of the acid in form of the acid tantalate of ammonium, while potassium ferrocyanide produces a yellow precipitate; ferricyanide, a white; and infusion of galls a light yellow precipitate, soluble in alkalies.

QUALITATIVE DETERMINATION.—Hydrochloric acid precipitates tantalum pentoxide, Ta_2O_5, at first, then redissolves it in excess.

Carbon dioxide, passed through a solution of an alkaline tantalate, precipitates acid or anhydrous tantalate.

Ammonium sulphide precipitates from a hydrochloric acid solution tantalic hydrate, TaO_2. OH, or an acid ammonium tantalate. Tartaric acid prevents the precipitation.

Ammonium chloride or sulphate precipitates tantalic hydrate.

Potassium ferrocyanide gives, when added to acidified solutions, a yellowish-white precipitate, which turns brown on the addition of a few drops of ammonia, and is soluble in larger quantities.

Potassium ferricyanide produces a yellow precipitate.

Infusion of galls, added to the solution of an alkaline tantalate, acidified by sulphuric or hydrochloric acid, forms a light yellow precipitate, soluble in alkalies.

Metallic zinc and hydrochloric acid do not reduce tantalum pentoxide, and no blue coloration (or only a very faint one) is observed.

QUANTITATIVE DETERMINATION.—Proceed as under niobium, including the treatment with ammonium sulphide, and remove the silicic and niobic acids, sometimes present, by dissolving the impure tantalic acid in a platinum dish by means of dilute hydrofluoric acid, filter, mix the contents of the filter with sulphuric acid, and evaporate to dryness. Ignite the residue and continue the glowing of the latter until its weight becomes constant. This operation will remove the silica. To effect the elimination of the niobic acid, dissolve the remaining mass in hydrofluoric acid, and add a boiling solution of acid potassium fluoride, so as to convert the tantalum into potassium fluotantalate, and the niobium into potassium fluoxyniobate. Evaporate on the water bath, when the former salt will gradually separate out on cooling; filter, wash the precipitate with water, till infusion of galls produces no longer an orange-colored coloration in a drop of the filtrate (which contains all the niobic acid), decompose the potassium fluotantalate by heating with sulphuric acid, boil the mass when dry with water to remove the potassium sulphate formed, filter and wash, and ignite the remaining tantalum sulphate strongly to decompose it. After cooling, weigh the tantalum pentoxide, Ta_2O_5, thus formed, which contains 81.98 per cent. of the metal, and calculate results.

In case other natural tantalates, like samarskite and euxenite, occurring in North Carolina, are to be analyzed, recourse may be had to the following procedure: Five grams of the "finely powdered" mineral are moistened in a platinum capsule with five c.c. of water, and then treated with ten c.c. of fuming commercial hydrochloric acid, which takes immedate effect upon the mineral in the cold, decomposing it in about ten minutes. The mixture is then heated on the water bath, until the excess of acid is expelled, when thirty to forty grams of water are added, and the mixture is filtered. The residue is thoroughly washed under the addition of one or two drops of hydrofluoric acid. The filtrate thus resulting contains all the metallic acids present, besides iron and manganese, and the residue remaining on the filter all the earths, as yttrium, cerium, thorium and uranium oxides. The separation of the several acids may then be accomplished according to the directions given above.

CHAPTER V.

MOLYBDENUM.

HISTORY.—It appears that the name "molybdenum" was derived from the ancient term molybdaena, which was applied by the Greeks and Romans to galena and other lead compounds. Until the middle of the eighteenth century molybdenite was considered as identical with graphite, then generally known as plumbago, or black lead, when the Swedish chemist Scheele showed in 1778 that it yielded a "white earth" on being oxidized with nitric acid, and that graphite did not produce such a body. His subsequent researches led to the correct idea, that the mineral was to be considered as a native sulphide. In 1782 Hjelm, a chemist of the same school, succeeded in isolating the metal by employing the trioxide for its production. He exposed the latter for that purpose to a full white heat in a crucible lined with charcoal, thus effecting its reduction to the metallic powder form, without, however, accomplishing the fusion of the latter into a metallic button, no means being known at that time for producing the degree of heat required to that end. Moissan, the prominent French chemist, was the first to reach this point in a satisfactory manner in 1893 by applying the heat of an electric furnace to a mixture of the dioxide and carbon, as described above.

CHEMISTRY AND COMMERCIAL POINTS.—Metallic molybdenum is a silver-white metal of atomic weight 95.9 and specific gravity of 8.6, and may be bought from the New York dealer in quantities of ten grams for one dollar. In the air it remains unchanged, and only combines with oxygen when heated to low redness. Hydrochloric or dilute sulphuric acid has no action on it, but aqua regia dissolves it readily.

In 1900 the production of metallic molybdenum in the United States amounted to 32,000 pounds, and that of ferromolybdenum to 11,000 pounds, which were valued at the place of production at $46,080 and $12,000 respectively. These products were obtained from ores which carried on the average fifty per cent of the metal and were sold at $240 per long ton.

In molybdenum we have a metal which forms one of the most remarkable compounds with steel, and this statement holds good still more extensively for an alloy ot molybdenum and nickel, when added to the former. The high fusing point of the metal (about 2,000° C.) has rendered the manufacture of molybdenum steel rather difficult, while the original procedure of applying it in the form of powder has led to repeated disappointments, since the finely subdivided metal oxidizes readily, when added to the fused steel. In fact it has been impossible in many cases to show the presence of the metal in the fused alloy, when thus prepared, by chemical analysis, so that the utilization of metallic molybdenum powders has been limited accordingly. On the market we find, nevertheless, powders of this kind containing from ninety to ninety-six per cent, of the metal, and the fused metal itself of ninety-four to ninety-eight per cent., both being yet used by certain manufacturers. Ferro-molybdenum is, however, largely preferred by the majority, and should be manufactured by adding the required percentage of molten metallic iron to fused and pure metallic molybdenum. Steel makers employ as a rule a ferro-molybdenum carrying fifty, seventy, seventy-five or eighty-five per cent. of the latter metal.

A fused molybdenum-nickel alloy has, however, been introduced lately, which is claimed to be superior to any other article of that kind in the market. This alloy contains, according to approximate analysis, seventy-five per cent. molybdenum with twenty-five per cent. nickel, or fifty per cent. molybdenum with fifty per cent. nickel, and outside of these two metals:

Iron	2.0 to 2.5 per cent.
Carbon	1.0 to 1.5 per cent.
Silicon	0.25 to 0.5 per cent.

When added in this form to molten steel, the nickel in the mass acts as a vehicle, and renders the alloy readily fusible, while the finished product shows a considerably improved elongation. The latter property has been increased in special cases from four to forty-five per cent. by applying the alloy, containing seventy-five per cent. of molybdenum and twenty-five per cent. nickel, which was added to the steel in such proportion as to obtain a final product carrying 0.25 per cent. molybdenum. An improved steel of this kind answers very well for the manufacture of all classes of forgings, as large cranks, propeller shafts, heavy guns, rifle barrels and plates for high pressure boilers, and especially for the construction of boilers for torpedo boats, where the maximum strength is required. It also finds application in the manufacture of shells, since an exceedingly hard and tough armor-piercing steel can be made from this alloy, while its increase in elongation renders it an excellent material for wire-drawing, for which purpose it answers better than any other alloy. It has also been found as a result of repeated trials that a molybdenum nickel steel of this composition is as hard as tungsten steel, but much less brittle, and that it will stand shocks in the lathe much better. Since tools made from such steel do not require grinding as often as those prepared from tungsten steel, the alloy must necessarily be of considerable value for makers of self-hardening tool steel.

In order to prepare molybdenum compounds or the metal itself from molybdenite, MoS_2, the mineral is powdered and placed in an open inclined crucible, which is heated to low redness in a charcoal fire, the mass being frequently stirred to facilitate the formation and escape of the sulphur dioxide formed. When these fumes cease to appear, the crucible is removed from the fire and allowed to cool, the remaining yellow powder being crude molybdic trioxide, MoO_3. The latter is then placed in a porcelain dish and covered with aqueous ammonia, which removes the trioxide in form of the ammonium salt and leaves the impurities behind. A further quantity of ammonium molybdate may generally be obtained from the residue by repeating the roasting process and the subsequent lixivation. On evaporating the solution thus resulting, the ammonium molybdate crystallizes out, and may be obtained as such, or the liquid is carefully neutralized with hydrochloric or nitric acid, so as to precipitate molybdic acid, which separates out as a white powder, scarcely soluble in water, but readily soluble in large excess of acid.

To produce metallic molybdenum from the ammonium molybdate, prepared in this manner, the latter is ignited, whereby the dioxide, MoO_2 is produced, which, when intimately mixed in the proportion of ten parts of oxide to one part of carbon, and subjected to the heat of an electric furnace, gives rise to the formation of a very pure metallic molybdenum. The mixture is allowed to be acted upon by the arc, produced by a current of 800 amperes and sixty volts, for only six minutes, so as to prevent the complete fusion of the sintered molybdenum, since, on continued action of the heat, the latter will unite with the carbon of the crucible in which the operation is performed. The metal obtained in this manner has a specific gravity of 9.01, is malleable as iron, can be forged and welded when hot, filed and polished with ease and takes up carbon by cementation.

Ammonium molybdate finds also application as a chemical reagent for the detection and estimation of phosphorus, since it forms a yellow double salt, known as ammonium-phosphomolybdate, in the presence of phosphoric acid. On the other hand sodium molybdate is employed for the decoration of crockery, as it produces stable and brilliant blue colors in the kiln fire. It furthermore serves for the dyeing of woolens and silks, the tints produced in this manner being reputed to be very attractive and durable.

MINERALOGY.—The most prominent molybdenum ore occuring in commercial quantities in Gunnison and Routt counties, Colorado, in New Mexico, Arizona, Washington and the eastern states Maine, New Hampshire, Vermont, Massachusetts, Pennsylvania, New York and Virginia is molybdenite, a sulphide of molybdenum, of the formula MoS_2. It resembles graphite in appearance, but is readily distinguished from it by the bluish-gray mark which it produces when drawn over paper, while graphite leaves a darker black imprint under these conditions. The difference between the two marks becomes strikingly evident when the two lines, made on paper by molybdenite and graphite, are drawn closely together. When passed over porcelain the streak produced by molybdenum appears olive green, and that of graphite gray. A further distinguishing test between the two minerals consists in covering a particle of each with nitric acid in test tubes, when, on heating, molybdenite will oxidize with the formation of the white or grayish molybdenum trioxide, MoO_3, while graphite remains unaffected. Before the blowpipe the mineral gives off vapors of sulphur dioxide, readily recognizable by their penetrating smell, while graphite burns under these conditions to carbon dioxide, which is odorless.

Molybdenite is very soft, hence stands low in the scale, its hardness varying between 1 and 1.5, and its specific gravity between 4.45 and 4.8. It occurs in granitic formations, quartz (British Columbia), mica and limestone, and is either disseminated through these rocks or forms separate veins or layers of foliated structure. Like graphite it is used as a lubricant for heavy work under high pressure, and is decidedly preferred to that mineral by manufacturers and engineers on account of its staying power. It changes by oxidation into the yellow oxide, MoO_3, also known as molybdic ochre, molybdine or molybdite, and occurs as such in considerable quantities near Telluride, Colorado. Characteristic specimens showing the transition of the sulphide into the oxide are frequently found, the oxygen of the atmosphere causing this gradual change.

Another molybdenum ore, known as wulfenite, a molybdate of lead, corresponding, when pure, to the formula $PbMoO_4$, deserves mention for the reason that it represents a naturally occurring metallic salt of molybdic acid. It occurs in well defined crystals of tetragonal, octahedral or tabular form, also in massive condition, and has a hardness lying between 2.57 and 3, and a specific gravity of 6.3 to 6.9. Its luster is resinous and its color varies from wax-yellow into orange, olive green, yellowish gray, grayish white and brown. The streak of the mineral is white, and its fracture subconchoidal. It is brittle, subtransparent, and assumes a darker color when heated, which disappears, however, on cooling. If the heating is continued the mineral fuses to a yellow mass, and leaves, when heated on charcoal before the blowpipe, globules of lead and a sublimate of molybdic oxide and trioxide. Hot nitric and hydrochloric acids, and also caustic potash, dissolve it. The mineral is found in small quantities at the Southampton lead mine in Massachusetts, in orange crystals at Wheatley's lead mine near Phœnixville, in the same state, and in Nevada, Arizona and New Mexico, but is not known to occur in commercial amounts.

Since molybdenite and molybdite occur in large deposits, which allow of commercial treatment in quantity, they can hardly be classed with the rare minerals, nor the metals contained in them with the rare metals. It seems, therefore, that of the metals mentioned so far in the preceding lines only niobium, thallium and tantalum can be justly arranged under that caption.

DETECTION.—A ready and reliable method of detecting molybdenum consists in pulverizing a sample of the ore to be tested to a fine powder, placing it in the lid of a platinum crucible, resting on a triangle, adding a few drops of concentrated sulphuric acid, and stirring the mass. When heating this mixture until copious white fumes of the acid are evolved, cooling and breathing repeatedly on it, a beautiful blue hydrous sulphate appears, which is readily distinguished. This coloration disappears on heating the lid, but returns on cooling and vanishes again on adding a sufficient quantity of water.

QUALITATIVE DETERMINATION.—Nitric or hydrochloric acid precipitates white molybdic acid, H_2MoO_4, from a concentrated solution of a molybdate, soluble, however, in a large excess of the acid.

Hydrogen sulphide gradually precipitates from acidulated solutions brownish-black molybdic trisulphide, MoS_3, soluble in alkaline sulphides or sulphosalts, which solutions are decomposed again by acids with precipitation of MoS_3, especially on the application of heat. On the addition of a little H_2S only, the molybdate solution acquires at first a blue tint; added in larger quantities it produces a precipitate, and the supernatant fluid appears green till on the addition of excess of H_2S the whole of the metal separates, though slowly, as trisulphide.

Ammonium sulphide gives a similar precipitate, soluble in excess.

Reducing agents, such as stannous chloride, mercurous nitrate, zinc and hydrochloric acid, produce changes, marked chiefly by alterations in color.

The principal and most characteristic reaction for molybdic anhydride consists, however, in precipitating it in a nitric acid solution, as yellow phospho-molybdate, or arsenio-molybdate, by the addition of a mere trace of soluble phosphate or arsenate.

QUANTITATIVE ESTIMATION.—Dissolve one or two grams of the molybdenum mineral to be analyzed in nitric acid and neutralize the solution thus obtained with excess of ammonia. Bring to a boil and filter. Make the filtrate slightly acid with hydrochloric acid, bring to a boil and add barium chloride to remove any sulphuric acid that may have been formed by the oxidation of the original sulphides. Filter off the barium sulphate. Now render the solution ammoniacal, bring to a boil and add a clear solution of lead acetate in slight excess. Boil for five minutes to render the precipitate granular and allow to settle. Filter, wash with hot water and dry at 100° C. Separate the precipitation from the filter, which is ignited. Add the precipitate and heat to redness; allow to cool and weigh. The residue contains 26.14 per cent. molybdenum.

In order to analyze an alloy of molybdenum, weigh off one gram of the substance, dissolve in 50 c.c. of aqua regia on the water bath, add hydrochloric acid as soon as complete solution has been effected, and evaporate to dryness. Treat the residue with dilute alcohol (fifty per cent.) and filter, when the greater part of the insoluble molybdic acid will remain on the tared filter. Evaporate the filtrate in the same manner as before, repeat the treatment with alcohol, and pass the solution containing an eventual precipitate through the filter used before. Dry at 100° C. and weigh The filtrate obtained in this manner serves for the determination of other metals present in the alloy.

CHAPTER VI.

TELLURIUM.

HISTORY.—In 1782 Mueller von Reichenstein, a German scientist, thought he recognized a peculiar metal in some specimens of gold ore occurring in Transylvania (Siebenbuergen), a province of Austria. Being doubtful about his discovery he sent some of the ore to the chemist Bergmann, who informed him that the unknown metallic body contained in it was different from stibnite (antimony sulphide), Mueller having intimated that it might eventually be identical with that mineral. As antimony occurs frequently in the European ores of this character, and tellurium resembles it in general appearance, the assumption was plausible. Not being able to obtain any positive result from Bergmann, the discoverer sent in 1798 samples of the ore to the prominent chemist and analyst, Klaproth, who confirmed the observations of Mueller, and called the new element tellurium from the Latin "tellus," meaning the earth. In 1832 the investigations of Klaproth were continued by the Swedish chemist Berzelius, who contributed largely to the knowledge of the compounds formed by the metal.

CHEMISTRY AND COMMERCIAL POINTS.—Tellurium is a brittle, silver-white metal of atomic weight 125, melting point 452°—455° C., and specific gravity 6.25, resembling sulphur in its degree of volatility and oxidation products, and partaking with the latter of the capability to impart very undesirable properties to most metals, when combined with them in any proportion. Thus the deleterious effect of tellurium upon copper, even when present in minute quantities, is very well known, and in combination with gold in the form of tellurides, it causes the precious metal to volatilize with its own vapor, if the ores are exposed to the heat of the assayer's furnace, so that special precautions are to be observed when testing them. On roasting these tellurides, the golden buttons, resulting usually after the evaporation of the tellurium contents of the ore are occasionally covered with a lead-gray coating, which is due to the formation of tellurous acid, and its subsequent combination with the ferric iron present. If tellurium or its compounds are introduced into the human system, they render the breath fetid by producing a strong garlic odor under the effect of the gastric juice. Tellurium appears, therefore, to represent the "black sheep" in the family of metals, and has in consequence not found any commercial employment as yet, though its electrical conductivity and resistance, which latter is very great, may lead to its application in that line in the future.

To produce metallic tellurium about 300 pounds of ore containing three per cent. tellurium is mixed in a cast iron pot with about 700 pounds sulphuric acid of 66° Beaume, and boiled for six hours. The next day the mixture is transferred to a lead lined tank and treated with about sixty-five gallons of hot water, when about forty pounds of commercial hydrochloric acid is mixed in during the next six hours. The following day the mass is filter pressed, and the solution containing tellurium passed into a lead lined wooden tank clamped up air tight, when it is digested with sulphurous acid for two or three days—whereby the tellurium in solution is precipitated in the metallic form—or until no precipitate is obtained on testing with sodium sulphite, which produces the same effect. The reactions taking place are as follows:

$$TeCl_2+SO_2+2H_2O=Te+2HCl+H_2SO_4.$$
$$TeCl_2+Na_2SO_3+H_2O=Te+2HCl+Na_2SO_4.$$

The Royal Hungarian Smelting Works of Schemnitz produces tellurium on a large scale, and puts it on the market in the crude and refined state, and in various forms at the following prices per kilogram (2.2 pounds avoirdupois) of actual tellurium, cash at Schemnitz; crude tellurium up to thirty per cent. of the element, 60 florins, or $21.60; thirty to sixty per cent, tellurium, 70 florins, or $25.20; sixty to eighty per cent. tellurium, 90 florins, or $32.40; eighty to ninety-five per cent. tellurium, 100 florins, or $36. Fused tellurium of ninety-four to ninety-seven per cent tellurium is worth 200 florins, or $72 per kilogram, and can be bought in sticks or granulated. Special turned tellurium sticks of different lengths, diameters and weight, suitable for scientific collections, can be obtained for 22 kreuzers, or 13 cents per gram.

The purification of crude tellurium is effected by conducting sulphur dioxide into a hydrochloric acid solution of tellurium dioxide, when a part of the tellurium is precipitated. On highly diluting this solution the remainder separates out completely. By fractionally precipitating the solution with sulphur dioxide, the tellurium can be obtained perfectly free from other elements.

To remove any sulphur or selenium eventually present the tellurium is heated in a current of hydrogen.

MINERALOGY.—Tellurium occurs native in the mineral kingdom, but more commonly in combination with gold, silver, lead and bismuth. Crystals of the native element have been found in Colorado, containing ninety-eight per cent of tellurium, with traces of gold, silver, copper and other metals, as shown by the following analytical data:

	Per cent.	Per cent.
Te	93.64	97.94
Au	2.18	1.04
Ag	1.15	0.20
Hg	1.34	None
Cu	0.34	None
Pb	1.02	None
Fe	0.18	0.89
Al_2O_3MgO K_2O	0.06	None
Total	100.00	100.07

Native tellurium has been found in the Keystone, Mountain Lion and Dunraven mines, Magnolia district; in the Smuggler mine, Ballarat district, and in the John Jay mine, Central district, all of them being situated in Boulder county, Colorado.

Among the naturally occurring tellurides the most prominent are sylvanite, calaverite, petzite, hessite and tetradymite. They were first found in Hungary and Transylvania, but later in larger quantities in the United States. Thus the state of Colorado is very rich in gold-silver tellurides, Boulder county and Cripple Creek, Teller county, being celebrated for the occurrence of such ores, while tellurous ores are found in considerable quantities in the Black Hills of South Dakota, and also in Montana and California.

Sylvanite or "graphic tellurium"—thus called on account of the triangular and rhombic figures resembling oriental characters, which mark the surface of the mineral—is a telluride of gold and silver, frequently associated with lead and antimony, of a pure steel-gray to silver-white or sometimes almost brass-yellow color. Its hardness varies between 1.5 and 2, and its specific gravity between 7.99 and 8.33. It occurs mostly disseminated and semi-crystalline, is very sectile, has an uneven fracture, and melts easily before the blowpipe, coloring the flame greenish-blue and covering the charcoal with a white coating of tellurous oxide. When heated further it finally leaves a ductile metallic globule.

The analytical results given below show the difference in constitution of foreign and domestic sylvanites, the former carrying antimony percentages varying from 0.58 to 8.54, and the latter being absolutely free from that element. This circumstance contributes also to explain the uncertainty of Mueller von Reichenstein as to the character of the then new element.

SYLVANITES FROM TRANSYLVANIA.

Te	59.97	44.54
Sb	0.58	8.54
Au	26.97	25.31
Ag	11.47	10.40
Pb	0.25	11.21
Cu	0.76	None
Total	100.00	100.00

SYLVANITE FROM COLORADO.

Te	58.91		52.96	
Sb	None	S	5.62	(Sulphur)
Au	29.35		26.39	
Ag	11.74		10.35	
Pb	None	Fe	4.45	(Iron)
Cu	None		None	
Total	100.00		99.77	

The occurrence of sylvanite was first observed in the Red Cloud mine at Gold Hill, Boulder county, Colorado, and later in the Grand View mine and other mines of that state.

The analysis of calaverite, a mineral found in association with sylvanite in the Keystone and Red

Cloud mines, led to the establishment of the following proportions:

Te	57.93
Au	39.01
Ag	3.06
Total	100.00

The mineral calaverite was originally discovered in the Stanislaus mine, Calaveras county, California, and received its name accordingly. It occurs in massive form, has a bronze-yellow color, a yellowish-gray streak, uneven subconchoidal fracture, and is remarkable for its brittleness. On charcoal it burns with a bluish-green flame, and yields globules of very yellow gold. Its gold contents dissolve in aqua regia, the silver remaining behind as silver chloride, AgCl.

The minerals petzite and hessite, belonging to the tellurides of silver and gold, are auriferous silver compounds, or rather natural alloys of the two metals, the former occurring prevalently in the Red Cloud mine, Colorado, and in the Stanislaus and Golden Rule mines of California. Like sylvanite and calaverite, petzite occurs mostly in massive form, shows a conchoidal fracture, metallic lustre, steel-gray to iron-black color and an iron-black streak. Its hardness equals the figure 2.51, and its specific gravity varies from 9 to 9 4. Its composition is represented as follows:

Te	31.64 to 34.16
Ag	40.60 to 42.36
Au	24.80 to 25.70

Hessite, which contains little or no gold, and corresponds to the formula Ag_2Te in general, is found in the Stanislaus mine, California, but always associated with native gold, quartz and altaite, a rare telluride of lead of the composition:

Te	37.31
Pb	60.71
Ag	1.17
Au	0.26
Total	99.45

The mineral hessite has a lead to steel-gray color, and occurs mostly massive and compact, but in cases fine grained and sometimes in granular form. Its hardness varies between 2 and 3.5, and its specific gravity between 8.3 and 8.6. It is sectile, of even fracture, and has a metallic lustre, its cleavage being indistinct. It analyzes as follows:

Te	38.07
Au	0.20
Ag	60.19
Cu	0.16
Pb	0.18
Fe	1.20
Zn	Trace
Total	100.00

Another telluride deserving mention is bismuth telluride or tetradymite, corresponding, when pure, to the formula Bi_2Te_3. It occurs in the Uncle Sam mine, Highland district, Montana, accompanied by gold and quartz; at the Red Cloud mine, Colorado; Montgomery mine, Arizona, and also in Virginia, North Carolina and Georgia.

Furthermore tellurium is known to occur in arsenical iron pyrites, and is found besides in the seleniferous mud of the sulphuric acid chambers.

DETECTION OF TELLURIUM IN TELLURIDES: Place a small fragment of the material, supposed to contain tellurides, in a porcelain dish, and add a drop of concentrated sulphuric acid. Heat gently and if tellurium is present a beautiful carmine color will appear instantaneously. This coloration is due to the formation of tellurous oxide, which dissolves in the sulphuric acid added, sulphur dioxide being evolved during the operation. On diluting the liquid with water the metal is reprecipitated as a gray powder.

In case the tellurium is associated with other minerals usually accompanying gold-bearing ores, treat the fine pulp with concentrated nitric acid in a porcelain dish and heat until the material is perfectly oxidized. Then add concentrated sulphuric acid, and heat until copious fumes of the acid appear, cool, add hydrochloric acid and water in about equal proportions, filter and add an excess of a solution of stannous chloride to the clear filtrate. In case tellurium is present the latter will be thrown down in the form of a flocculent black precipitate of metallic tellurium.

DETECTION OF TELLURIUM IN BULLION: On testing bullion for the presence of tellurium, the best method consists in boiling a finely pulverized sample, obtained by filing and sifting, with a concentrated solution of caustic potash or soda with the addition of powdered zinc, when the solution assumes the characteristic amethystine color, if tellurium is present.

Tellurium is readily distinguished from selenium, which it closely resembles, by its behavior before the blowpipe, since tellurium emits only a faintly acid odor when thus treated, while the presence of the slightest trace of selenium produces a powerful odor resembling that of decayed horseradish.

QUALITATIVE DETERMINATION.—Telluric Compounds: Hydrochloric acid does not decompose tellurates in the cold, but on boiling the solution chlorine is evolved, and on dilution with water tellurous acid, H_2TeO_3, is precipitated, soluble only in a considerable excess of hydrochloric acid. This behavior distinguishes tellurium trioxide from the dioxide.

Tellurous Compounds: Hydrochloric acid decomposes solutions of this kind and precipitates white tellurous acid. Tellurium resembles in this respect antimony and bismuth compounds.

Hydrogen sulphide precipitates from acid solutions brown tellurous sulphide, TeS_2, resembling in color stannous sulphide, SnS, and very freely soluble in ammonium sulphide.

Reducing agents as Na_2SO_3, $SnCl_2$, metallic zinc and hydrochloric acid, and a solution of sulphurous acid, reduce tellurium compounds and precipitate black metallic tellurium, which is insoluble in an aqueous solution of potassium cyanide.

QUANTITATIVE ESTIMATION.—Dissolve one gram of the tellurium ore in hydrochloric acid, and if this should not be feasible, in nitric acid, which latter reagent must, however, be removed by the subsequent addition of hydrochloric acid and heating, since the presence of nitric acid causes the reoxidation of a part of the precipitated metallic tellurium obtained in the course of the process. Filter, concentrate by evaporation and add to the heated (not boiling) liquid gradually an alkaline solution of sodium sulphite, or conduct sulphur dioxide through it when cold. Collect the black-gray metallic tellurium thus precipitated on a tared filter, and dilute the filtrate strongly with water. Bring any tellurium separating out on prolonged standing on the filter used before, wash, dry the latter with its contents at a gentle heat and weigh.

CHAPTER VII.

PLATINUM AND THE PLATINUM METALS.

HISTORY.—In the year 1735 metallic platinum was brought to Spain from South America by Ulloa, a Spanish traveler who obtained the specimens from the gold-bearing sands of the river Pinto, in the district of Choco, near Papayan, in the United States of Colombia. About six years later a certain Mr. Wood, who traveled in Jamaica, acquired some of the metallic nuggets and presented them in 1750 to the English chemist Watson for examination. The latter recognized the presence of until then an unknown metal in these nuggets, which fact was confirmed by the subsequent researches of the director of the Stockholm mint, Scheffer. He declared the metal to be "white gold," called in Spain platina del pinto, from plata, meaning silver, the diminutive being platina, which term lead to its present appellation, "platinum." Later researches showed that besides the predominating platinum contents, there were other metals alloyed with the natural product. Thus the English chemist, Wollaston, proved in 1803 the presence of two other distinct metals in the ore, which he called palladium and rhodium. These names are derived respectively from the asteroid Pallas, discovered in

1802, and from the Greek noun "rodon," meaning rose, since certain solutions of rhodium salts have a roseate color. In the same year the French chemist Tennant discovered besides these, yet two further metals in platinum ore, which he named iridium, from the iridesence of some of its solutions, and osmium on account of the penetrating chlorine-like smell given off by osmium tetroxide, the Greek term, having served for its derivation, being "osma," meaning smell or odor. Finally the German chemist, Claus, detected in 1845 a fifth metal in platinum ore, which he called ruthenium from the country of Ruthenians, a Little-Russian people, the ore tested having been found in the Ural mountains.

Some chemists pretend, however, to have established the presence of a sixth metal besides platinum in the ore which has been named Davyium, symbol Dm., in honor of the great English chemist, Humphrey Davy. It is described as having the atomic weight 154, though this point is somewhat doubtful, and as occurring in minute quantities in some platinum ore. Davyium has been obtained, precipitated on zinc, from the residues remaining after the separation of iridium and rhodium, and appears to be a white metal, which decomposes water in presence of sulphuric acid, the oxide formed scarcely dissolving in the acid. It combines with sodium chloride to produce a double salt, which is very insoluble in water. The discovery of Davyium in platinum ores was made by the prominent chemist, Sergius Kern.

CHEMISTRY AND COMMERCIAL POINTS.—Platinum of atomic weight 195 and specific gravity 21.5 is a rare metal, and there is every indication extant that it will be classed with that category for a long time to come. The metal itself, when in pure condition, is of a tin-white color, extremely ductile, and, next to gold and silver, the most malleable metal known. Its fusing point lies at 1,750° C., and this property, together with its resistance to oxidation at high temperatures, makes it an indispensable article for the preparation of chemical apparatus, as dishes, crucibles, foil and wire. Furthermore it is not affected by nitric, hydrochloric or sulphuric acids in cold, but by free chlorine and bromine at ordinary temperatures, the formation of platinic chloride and bromide being the final result. Heated platinum vessels are also attacked by free sulphur, phosphorus, arsenic, selenium and iodine, so that the fusion of sulphides, sulphates and phosphates with reducing agents is detrimental to platinum crucibles or dishes. Organic substances containing phosphates, ferric chloride, alkaline cyanides, potassium nitrate, bromides, iodides, alkali hydrates, alkaline earths, and especially barium and lithium hydrates, when ignited in platinum vessels in the air, corrode the latter gradually. Most harmful in this respect are the metals lead, bismuth, tin, mercury, antimony and zinc, or their compounds, which act almost immediately, when heated in a platinum crucible, and form readily fusible alloys. Platinum vessels, which have been tarnished by constant use, are preferably cleansed by fusing borax in and upon them, or by digestion with nitric acid. The best support for these vessels is the triangle made of platinum wire. The metal itself is completely dissolved, when heated with aqua regia, under the formation of platinic chloride, $PtCl_4$, the solution thus obtained being largely used as a reagent in chemical laboratories.

In 1905 the production of metallic platinum in the United States amounted to 305 ounces, the main part of which was recovered at the San Francisco mint by parting and refining the gold washings received from Trinity, Shasta and Plumas counties, California. British Columbia and the Sudbury district, where the nickel matte produced in the smelting works carries platinum values, contributed also to the output to some extent.

The world's production in platinum for 1900 amounted to about 165,000 ounces, of which Russia contributed 153,000 ounces, while the imports were valued at $1,762,020. The demand for platinum outranks the supply sufficiently to maintain the price of platinum ore at a figure approaching that of gold, eventual vacillations in the market being caused by the more or less successful production of the Russian mines. New York prices for 1900 were $18.50 per troy ounce for ingots, and 72 cents per gram for crucibles, hammered ware and wire.

The manufacture of platinum from its ores is carried on by digesting the mineral with dilute aqua regia to dissolve the gold, if present, and then treating the remaining mass with stronger aqua regia, often under pressure when platinum with traces of iridium and rhodium enter into solution as chlorides. The residue consists chiefly of earthy impurities, and of an alloy of osmium and iridium (osmiridium), which is not attacked by aqua regia. The solution is evaporated to dryness, the remainder digested with water, filtered, and the clear liquid mixed with a solution of ammonium chloride. A yellow crystalline double salt, known as ammonium platinic chloride, is thus produced, which is insoluble in alcohol and slightly soluble in water. It separates out, therefore, from the solution on the addition of alcohol, when it is filtered off, washed with alcohol, dried and then heated to redness. After this treatment metallic platinum remains behind in form of a gray, spongy mass, known as platinum sponge. This material, when welded into a compact mass under strong pressure and at a high temperature, is used for the preparation of platinum vessels, but contains still traces of iridium and rhodium, which are, however, desirable adjuncts, since they contribute greatly to increase the toughness, tenacity and resistance of the metal, and render it more suitable for the manufacture of platinum vessels.

When manufacturing platinum on the large scale, the crude ore is treated in a reverberatory furnace with an equal weight of galena, when the platinum forms an alloy with the lead, which is reduced to that condition from the sulphide by the iron present in the mineral. Ground glass and borax are then added as fluxes, when the osmiridium, which does not alloy with the lead, settles gradually to the bottom in consequence of its high specific gravity. An addition of litharge is then made, in order to oxidize the sulphur, and finally the slag is skimmed off, and the metal run into ingots, which, upon cupellation, yield platinum containing some iridium and rhodium. This product may be purified further, but answers for ordinary purposes, where small quantities of iridium and rhodium are rather welcome, as pointed out before. The cost of preparing these ingots is about 20 cents per kilogram of ore treated, when working on 100 kilogram lots.

MINERALOGY.—The occurrence of platinum in nature resembles that of gold to some extent, since it has been found so far in paying quantities mostly in alluvial deposits. The metal accompanies frequently the gold contained in auriferous sands of rivers, and occurs then in form of grains and scales, or in round, flattened or irregular lumps and nuggets. It is assumed, therefore, that platinum is a product of erosion, like alluvial gold, and that it was washed out of the rocky strata and deposited in the river beds in the course of eons. The United States of Colombia, St. Domingo, Brazil, Mexico, Borneo, New Zealand, New South Wales and British Columbia are known to contain platinum deposits, while the metal occurs besides in combination with arsenic as sperrylite near Sudbury, in Ontario province, Canada. In the United

States it has been found in traces with gold in Rutherford county, North Carolina; in the gold washings of the Klamath region at Cape Blanco, and in those of Cherokee, Butte county, California, but not in abundance. Oregon and Alaska are also limited and occasional producers. A remarkable find made near Plattsburgh, New York, was that of a mass weighing 104 grams, of specific gravity 10.45, and consisting of forty-six per cent platinum and fifty-four per cent chromite.

The eastern declivity of the Ural mountains in Russia represents, however, the most prolific source of the metal. It is obtained there by washing the platiniferous sand, containing at the most its three-thousandth part in platinum. The grains of the ore are as a rule very small, and the finding of larger lumps or nuggets belongs to the rarities. Since the complete separation of the metallic grains or scales from the accompanying specifically heavy minerals cannot be effected at the place of occurrence in the Ural mountains, the ore brought into the market, is usually mixed with titaniferous, magnetic and chromic iron, zircon, spinel, quartz and iron and copper pyrites, the whole being reduced to a fine sandy mass. To specify this point more clearly, it may be said that platinum ores contain: 1. Sand, which can be only partly removed by washing with water, and contains quartz, zirconium, iron chromate and, in the Russian ores, iron titanate. 2. Osmiridium. 3. Platinum, iridium, rhodium, ruthenium and palladium, combined in the form of an alloy. 4. Copper and iron in the metallic state. 5. Gold, and frequently silver. The latter metal is generally found with the palladium. The platinum grains, contained in this mixture, carry, as a rule, from seventy-five to eighty-seven per cent. of that metal, besides a quantity of iron, sufficient to render them magnetic, from one-third to one per cent of palladium, but sometimes much less, with smaller quantities of copper, rhodium, osmium, iridium and ruthenium. The mother rock in which platinum ores occur consists usually of serpentine, probably altered into the latter from peridotite, a magnesium iron silicate, intimately related to chrysolite, which is often partly changed to serpentine. The ore has been discovered in considerable quantities lately in the Philippines, and in the Copper river district of Alaska, in which latter locality it is said to possess a value of $13 per ton at the surface, increasing with depth, and in the New Rambler mine of the Grand Encampment district, Wyoming, about December, 1901. This ore is reported to carry 1.5 to 6.8 ounces of platinum per ton, and the matte from the Grand Encampment smelter 4.84 ounces of the metal. Professor Wilbur C. Knight of the Wyoming State University has investigated the case more closely, having besides had analyses made by three of the leading mineralogists in the United States, and reports that the ore in question carries from ten to twelve ounces of platinum and palladium, worth approximately $25 per ounce, and from eighteen to twenty-five per cent copper. The ore runs from $275 to $400 per ton in platinum, palladium and copper.

Analyses of the California and Oregon ores gave the following results:

	California.	Oregon.
Platinum	85.50	51.45
Iron	6.75	4.30
Palladium	0.60	0.15
Rhodium.	1.00	0.65
Iridium	1.05	0.40
Osmium.	None	None
Copper	1.40	2.15
Osmiridium	1.10	37.30
Gold	0.80	0.85
Sand	2.95	3.00
Totals	101.15	100.25

DETECTION.—Dissolve in a casserole five grams of the platinum ore by means of aqua regia, evaporate to dryness on the water-bath, and heat the residue gently until every trace of nitric acid is expelled. Take up with water, filter and add to the clear liquid a few drops of potassium iodide solution, when the platinum iodide formed will dissolve, producing a deep rose-colored liquid, which resembles closely a solution of cobaltic nitrate. The addition of a few drops of acid to the colored solution hastens the appearance of the color, while heating causes it to disappear. Hydrogen sulphide, sodium sulphite or sodium thiosulphate (hyposulphite), sulphurous acid, and mercuric chloride have the same effect upon the liquid as heat.

QUALITATIVE DETERMINATION.—Platinous chloride of the formula $PtCl_2$ is a greenish brown powder, which dissolves to a dark brown solution in hydrochloric acid. A solution of the salt remains in the platinous condition as long as the access of air is excluded from it, but changes to the platinic state when brought in contact with the latter. Caustic potash or soda precipitate from a platinous solution the hydrate $Pt(OH)_2$ of a dark brown color, soluble in excess of the reagents as potassium or sodium platinite of the composition K_2PtO_2 and Na_2PtO_2 respectively. Addition of alcohol to the liquid causes the precipitation of platinum black. Ammonia throws down a green crystalline precipitate of platinous ammonium chloride, $PtCl_2.2NH_3$, which is insoluble in alcohol and cold water. Hydrogen sulphide precipitates very slowly the black platinous sulphide PtS, which is sparingly soluble in water and ammonium sulphide, and is not affected by acids. Potassium iodide precipitates slowly platinous iodide of the formula PtI_2, whose color lies between red-brown and black. Oxalic acid produces no change in platinous solutions, while ferrous sulphate reduces them gradually, and metallic zinc causes rapid reduction.

Platinic chloride of the formula $PtCl_4$ forms a brownish-red liquid, when dissolved in water or alcohol, and produces, on the addition of caustic potash, soda or ammonia to its concentrated solution, a yellow crystalline precipitate of potassium, sodium or ammonium platinic chloride of the compositions $PtCl_4.2KCl$; $PtCl_4.2NaCl$; and $PtCl_4.2NH_4Cl$ respectively. This precipitate is slightly soluble in water, insoluble in alcohol, but soluble in excess of alkali, and is reprecipitated from such solutions by hydrochloric acid. Addition of ammonium chloride causes the precipitation of ammonium platinic chloride. Hydrogen sulphide and ammonium sulphide precipitate slowly the black platinic sulphide, PtS_2, which is slightly soluble in water, also dissolved by chlorine, and in excess of ammonium sulphide as ammonium sulphoplatinate. Potassium iodide colors the solution brown-red, and precipitates the black platinic iodide, PtI_4. Excess of the reagent causes the precipitation of potassium platinic iodide of the formula K_2PtI_6 or $PtI_4.2KI$, of a brown color, which is slightly soluble in water. The reduction of platinic solutions to metallic platinum cannot be effected by the addition of oxalic acid, but is accomplished gradually on giving ferrous sulphate to the liquid, and speedily by means of zinc or iron.

QUANTITATIVE ESTIMATION.—Bring from two to five grams of the ore into solution by means of aqua regia, evaporate to dryness, take up with hydrochloric acid and hot water, filter, wash and conduct hydrogen sulphide through the filtrate to saturation. Let stand for twenty-four hours, filter off the sulphides, wash them with water containing hydrogen sulphide, and dissolve them in a little aqua regia. Dilute, filter off the sulphur separated out, if necessary, and add to the acid liquid a saturated solution of ammonium chloride and sufficient alcohol to render the precipitation of the ammonium platinic chloride complete. Filter, wash the precipitate with water to which a little ammonium chloride has been added besides some alcohol, and bring the moist filter, containing the precipitate, into a crucible, cover with the lid, and heat gently till the mass is charred. Then apply stronger heat to drive off the chlorine and ammonium chloride, and finally open the crucible partly, so as to burn away the carbonaceous residue. Cool and weigh as metallic platinum. The precipitate may contain traces of double salts of other platinum metals, and should be tested according to the directions given in the following chapters.

A method suitable for the recovery of platinum from photographic or laboratory residues, consists of the following operations: Heat the neutral solution containing the platinum to boiling, and add, while the liquid is in ebullition, a saturated solution of sodium carbonate, mixed with one-third its volume of glycerine, when all the platinum present will be precipitated in the metallic state. Filter, wash, dry, incinerate and weigh. It is essential that the sodium carbonate added be in excess. If iron or other metals are present, the precipitate should be digested with dilute acid to remove them. Paper residues must be burned first, and incinerated subsequently in the muffle, before they are digested with aqua regia, and the solution resulting is treated with ammonium chloride.

CHAPTER VIII.

PALLADIUM.

CHEMISTRY AND COMMERCIAL POINTS.—To this category belong the metals palladium, rhodium, osmium, ruthenium and iridium. The first of them, palladium, has the atomic weight 106, and a specific gravity of 11.4. It occurs native in platinum ores, principally, however, alloyed with gold and silver in Brazilian gold ore, and is said to have been found also in St. Domingo and the Ural mountains. The gold ore from Brazil contains, as a rule, from five to ten per cent. of metallic palladium, and the metal is obtained from the gold dust by fusing it together with silver, and dissolving the granular alloy thus obtained in nitric acid under the application of heat, when only silver and palladium enter in solution, and the gold remains. By the addition of salt solution to the liquid separated from the gold, the silver is precipitated as chloride, which is removed by filtration, and the palladium contained in the filtrate then precipitated by means of mercury cyanide as a yellowish-white gelatinous precipitate of palladous cyanide, which leaves on ignition spongy metallic palladium.

To recover the palladium from platinum ore, the latter is treated with aqua regia, the acid solution filtered from the insoluble residue, and excess of ammonium chloride and alcohol added to the filtrate to precipitate platinum and iridium. The precipitate having settled, the liquid is filtered, the former washed with ammonium chloride and alcohol, and the palladium thrown down from the filtrate by mercury cyanide.

Palladium has the lowest melting point of all platinum metals, 1500° C., resembles platinum in lustre, and approaches steel in hardness. It is more malleable than platinum, can be more readily welded than the latter, and shows, when polished, a whitish steel-like lustre, which does not tarnish. When fused to a button it absorbs oxygen from the atmosphere, evolving it on cooling, when it sprouts like silver, and becomes very porous. Tincture of iodine blackens the surface of palladium, but not that of platinum. On account of its great resistance to oxidation by atmospheric oxygen and moisture, and to the effect of sulphuretted gases, it is employed for the inner mechanism of chronometers and watches, also for the construction of fine balance beams, for the divided scales of delicate apparatus, and for surgical instruments. Both platinum and palladium find application in photography for the preparation of toning baths. When fused with gold in the proportion of one to six, palladium forms a white alloy, which was employed for the graduated part of the mural circle, constructed for the observatory of Greenwich.

Palladium has the peculiar property of absorbing or occluding hydrogen at ordinary temperatures, and more so when heated. Thus freshly ignited palladium foil takes up more than 370 volumes of hydrogen at usual temperatures, and about 650 volumes of the gas when heated to from 90 to 100° C. Under such condition the metal forms first palladium hydride, Pd_2H, absorbs subsequently the rest of the hydrogen, becomes specifically lighter, and expands to one-tenth its volume, but retains its metallic appearance. This phenomenon may be shown to best advantage by attaching a piece of palladium in sheet or wire form to the negative pole of a battery, when decomposing water by the electric current, as the hydrogen thus disengaged will then be absorbed by the palladium. Palladium-black and spongy palladium possess the property of absorbing hydrogen to a yet higher degree than the compact metal, since the former takes up at 100° C. upwards of 980 times its volume of the gas, and spongy palladium, when heated in the air until the white metallic luster becomes black-colored, absorbs hydrogen with avidity, and even oxidizes it partly to water

DETECTION. Mix a solution of sodium thiosulphate in a test tube with a little ammonia, and add a drop of the solution of the ore supposed to contain palladium, so as to color the liquid a pale lemon-yellow. Boil and observe the changes in coloration from a wine-brown shade to black. By dilution with water the liquid assumes its former brown tint, but does not become turbid.

Qualitative Determination.—Water precipitates a brown basic salt from solutions containing slight excess of acid only.

Hydrogen sulphide or ammonium sulphide throw down from acid or neutral solutions black palladous sulphide, PdS, insoluble in ammonium sulphide, but soluble in boiling hydrochloric acid and readily soluble in aqua regia.

Potassium or sodium hydrate precipitate a yellowish-brown basic salt, soluble in excess.

Soluble carbonates precipitate brown palladous hydrate, $Pd(OH)_2$, soluble in excess, reprecipitated on boiling.

Ammonia or ammonium carbonate produce no precipitate from the nitrate, but decolorize the dark brown solution.

Hydriodic acid or soluble iodides give, even in very dilute solutions, a black precipitate of palladous iodide, PdI_2, somewhat soluble in excess of potassium iodide. (Most characteristic reaction for palladium. It serves for the detection of iodine in the presence of chlorine or bromine.)

Mercury cyanide gives a yellowish-white gelatinous precipitate of palladous cyanide, readily soluble in potassium cyanide and in ammonia, slightly soluble in hydrochloric acid. It leaves on ignition spongy metallic palladium.

Ammonium sulphocyanate gives no precipitate, even after the addition of SO_2. (Distinction from copper.)

Stannous chloride produces a brownish-black precipitate, soluble in hydrochloric acid to an intense green solution.

Palladous salts are reduced to the metallic state by phosphorus, sulphurous acid, potassium nitrite, formic acid, metallic zinc or iron, and alcohol.

Palladous chloride, obtained by dissolving palladous sulphide in boiling hydrochloric acid, is precipitated by ammonia as flesh-colored ammonium-palladous chloride, $PdCl_2.2NH_3$, soluble in ammonia to a colorless liquid, from which hydrochloric acid precipitates it as a yellow crystalline chloride, identical in composition. Palladium shows a strong tendency to form compound ammonias.

Ammonium chloride does not precipitate palladium salts. Potassium chloride precipitates a brownish-red octahedral double chloride, $PdCl_2.2KCl$, insoluble in absolute alcohol, and soluble in water to a dark-red liquid.

All palladium salts are decomposed by ignition, leaving metallic palladium.

QUANTITATIVE ESTIMATION.—The quantitative estimation of palladium is executed according to the directions given under "Chemistry and Commercial Points," and referring to the recovery of palladium from the ores. Palladium is separated from copper by saturating the solution containing the two metals with sulphurous acid, and adding a solution of potassium sulphocyanate. This reagent has no action on palladium, while it completely precipitates the copper in the form of a white sulphocyanate.

CHAPTER IX.

RHODIUM.

CHEMISTRY AND COMMERCIAL POINTS. — RHODIUM: The metal rhodium of atomic weight 104, specific gravity 12.1, and fusing point 2000° C., is a whitish-gray metal, less malleable or ductile than platinum, unalterable in the air at ordinary temperatures, but oxidizable at a red heat. When pure it resists the action of the strongest acids, even that of aqua regia, but when alloyed with lead, bismuth, copper or platinum it dissolves in that liquid. On the other hand it does not dissolve in aqua regia, when alloyed with gold or silver. It sprouts or spits like silver, when heated and gradually cooled after fusion.

Rhodium is contained in the solution remaining after the precipitation of platinum, and the metals in solution are thrown down together from the liquid by means of metallic iron, when the mass, obtained in this manner, is mixed with one part of lead and two of litharge, and fused. From the fusion the lead, copper and palladium are removed by dilute nitric acid, and the residue is heated to redness for two hours with five parts of barium oxide. The mass is then cooled, lixiviated with water, and the residue boiled and distilled with aqua regia to remove osmium. The remaining solution is treated with sulphuric acid, decanted from the precipitated barium sulphate, evaporated at 100° C. with excess of ammonium chloride, and washed with a solution of ammonium chloride until the washings show no longer a red coloration. The filtrate and washings are evaporated with sufficient nitric acid to decompose the ammonium chloride, and the residue is heated to redness with three or four parts sulphur. Pure rhodium remains on boiling the residue with aqua regia and sulphuric acid.

The metal or its compounds have as yet found no special commercial application, and have therefore but limited interest.

DETECTION.—Convert the rhodium obtained according to directions given under "Chemistry and Commercial Points" into the ammonium double chloride, wash the precipitate repeatedly with ammonium chloride, and then evaporate the double salt of rhodium, thus resulting, with ammonia. In this manner the rhodium is converted into the chloride of the ammonium-rhodium base, which should be purified by crystallization. Rhodium is found in small quantities in platinum ores, and often to considerable extent in platinum residues. Its salts are for the most part rose-colored and hence readily recognized.

QUALITATIVE DETERMINATION. — Hydrogen sulphide or ammonium sulphide precipitate from a hot solution brown rhodic sulphide, Rh_2S_3, insoluble in ammonium sulphide, but soluble in boiling nitric acid.

Potassium or sodium hydrate give with the double chloride of sodium and rhodium a yellowish-brown precipitate of rhodic hydrate, $Rh_2(OH)_6$, soluble in excess; in other rhodic salts this precipitate appears only on boiling.

From a solution of rhodic chloride, potassium hydrate produces at first no precipitate, but gives, on the addition of alcohol, a brown precipitate of rhodic hydrate.

Ammonia gives also a yellow precipitate, only formed, however, after some time. It is soluble in hydrochloric acid.

Potassium iodide causes the formation of a slight yellow precipitate.

Metallic zinc precipitates black metallic rhodium.

Potassium nitrite gives with the chloride an orange yellow precipitate, which is slightly soluble in water, and only very slowly decomposed by strong hydrochloric acid. (Characteristic.)

Rhodium is further distinguished from the other platinum metals by its insolubility in aqua regia, its solubility on fusing it with acid potassium sulphate, and the behavior of its chloride with potash and alcohol.

QUANTITATIVE ESTIMATION.—Dissolve the ore in aqua regia, remove the platinum and iridium by precipitation with ammonium chloride and alcohol, and throw down the palladium by means of mercury cyanide. Saturate the filtrate with sodium carbonate, add hydrochloric acid to decompose the excess of the cyanide, evaporate to dryness, and treat the residue with alcohol. Under this treatment only the sodium chloro-rodiate will remain as a red-brown powder, while the rest of the mass dissolves. This salt, when heated in a current of hydrogen, and washed with a large quantity of water, yields pure rhodium.

CHAPTER X.

OSMIUM.

CHEMISTRY AND COMMERCIAL POINTS.—Osmium has the atomic weight 192, a fusing point approaching 2500° C., and the high specific gravity 21.4, which figure shows it to be the densest of all metals. Its separation from osmiridium, which remains on dissolving the platinum ore in aqua regia in the form of white, metallic looking hard grains, depends on its property of forming a volatile tetroxide. Taking advantage of this point, the "powdered" osmiridium is mixed with one part of sodium chloride, and exposed in a glass tube to a current of dry chlorine gas at dull redness, when the double chlorides of the two metals are formed. The reduction of the osmiridium to powder form is best effected by fusing it with zinc and a small amount of ammonium chloride, when the two metals contained in the natural alloy will combine, and the zinc is dissolved from the cooled mass by means of dilute sulphuric acid, osmium and iridium remaining as impalpable powders. The mass, containing the double chlorides, is then allowed to cool, dissolved with boiling water, the solution concentrated by evaporation, acidulated with nitric acid, and distilled from a retort, until the whole of the osmium has volatilized, the iridium remaining behind as the double chloride, $IrCl_4$ 2KCl. This salt is obtained in reddish-black regular octahedra by recrystallizing from water. The fumes of osmium tetroxide, volatilizing from the mixture, are conducted into a receiver containing a solution of caustic potash, and the alkaline solution thus obtained is evaporated with an excess of ammonium chloride, which leaves on ignition of the dry residue, and washing with water, metallic osmium in form of a black or gray powder, possessing metallic luster. The solution of the iridium salt remaining in the bulb of the retort is concentrated, also treated with ammonium chloride, and the precipitated iridium ammonium chloride ignited, when it forms spongy iridium.

Another procedure of treating the solution of osmium tetroxide consists in precipitating the osmium as sulphide by means of ammonium sulphide, washing and drying the latter, and placing it in a gas-coke crucible resting within a fireclay crucible, whose cover is carefully luted on, and heating the whole for four hours to about 1600° C. The metal obtained in this manner may be rendered denser by heating it at the temperature of a very powerful electric arc, which appears to be the best adapted apparatus for operations of this kind. When fused in this manner it presents a brilliant metallic surface of a beautiful blue color, slightly tinged with gray. The fumes of osmium tetroxide are remarkable for their extremely poisonous nature and offensive odor, the latter resembling that of chlorine or iodine, so that all operations of this kind should be performed under a well-drawing hood. These vapors are absorbed by water, and metallic osmium is precipitated from such a solution in form of a black powder by most metals, including mercury and silver. When osmium is heated with five or six per cent tin at bright redness it dissolves in the latter, and if the cooled alloy thus resulting is treated with hydrochloric acid, the metal remains in form of a hard, crystalline powder of specific gravity 22.48, the highest observed for the metal.

The utilization of osmium or its compounds is limited at present to the preparation of filaments for incandescent lights, and the precipitation of bacterial organisms from water or other liquids.

DETECTION.—All osmium compounds, when boiled with an excess of nitric acid, give off a pungent odor of the tetroxide, OsO_4.—Mix the mineral to be tested with salt, and heat the mixture, placed in a porcelain boat, in a tube of hard glass, while conducting moist chlorine over it. Conduct the fumes of osmium tetroxide, formed under these conditions, into a solution of caustic potash, add excess of ammonium chloride, and evaporate the mixture to dryness. Ignite the dry residue, filter, wash with water and dry to obtain metallic osmium.

QUALITATIVE DETERMINATION.—Hydrogen sulphide and ammonium sulphide produce a brownish-black precipitate of osmium sulphide, OsS, which only separates out when a strong acid is present. The precipitate is insoluble in ammonium sulphide.

Potassium hydrate, sodium hydrate or potassium carbonate produce a brownish-red precipitate of hydrated osmium dioxide. $Os(OH)_4$.

On fusing the double chloride with sodium carbonate, dark grey OsO_2 is obtained.

Heated with tannic acid, or alcohol, under addition of hydrochloric acid, the double chloride is reduced to the blue osmious chloride, $OsCl_2$.

A solution which contains osmic acid (an osmate) is remarkable for its great oxidizing power. It decolorizes indigo solution, separates iodine from potassium iodide and converts alcohol into aldehyde and acetic acid. Sodium sulphite yields a deep violet coloration, and dark blue osmious sulphite, $OsSO_3$, gradually separates. Ferrous sulphate produces a black precipitate of OsO_2. Stannous chloride produces a brown precipitate, soluble in hydrochloric acid to a brown liquid. All compounds of osmium yield the metal when ignited in a current of hydrogen.

QUANTITATIVE ESTIMATION.—This operation is executed according to the directions given under "Chemistry and Commercial Points."

CHAPTER XI.

RUTHENIUM.

CHEMISTRY AND COMMERCIAL POINTS.—Fused ruthenium is a hard brittle metal of atomic weight 101.7 and specific gravity 11.4, its melting point lying near 2500° C., and is found in small quantity in that portion of the platinum ores which remains behind after treatment with aqua regia. It is a grayish-white substance, closely resembling iridium, which oxidizes slowly in air, and when heated, covers itself with bluish-black ruthenic oxide of the formula Ru_2O_3. If heated in an atmosphere of oxygen, it burns with a smoky flame, brilliant sparks being emitted, which phenomena are accompanied by the generation of an odor resembling that of ozone. Ruthenium is scarcely affected by acids or aqua regia, but combines with chlorine at a red heat. To produce the tetroxide of the metal, chlorine gas is passed through the heated alkaline solution of a ruthenium salt, contained in a retort, when the volatile tetroxide distills over. It forms golden-yellow crystals, melting at 85° C. and boiling at about 100° C., which decompose with explosion, when heated to 108° C. The metal ruthenium is prepared on a larger scale from the residue remaining after treatment of platinum ores with aqua regia by reducing the latter to a fine powder, which is effected by fusing it with zinc and a little ammonium chloride, and treating the resulting mass with dilute hydrochloric acid to remove the zinc. The powder is then heated with a mixture of three parts barium oxide and one part barium nitrate to about 950° C., and the cooled mass brought into a stoppered and cooled flask, so as to prevent the escape of osmium oxide. When all action has ceased, one part nitric and two parts sulphuric acid are added, the mixture is shaken, allowed to settle, and the solution thus obtained decanted from the barium sulphate formed. The liquid is then subjected to distillation, the whole of the osmium being contained in the distillate. The equally volatile ruthenium tetroxide is not produced under these conditions. To the residue are added two or three parts of ammonium chloride and a little nitric acid, the liquid is evaporated on the water bath, and washed with a mixture of one part saturated ammonium chloride solution and one part water, when the washing is continued until the filtrate is colorless. The residue consisting of ammonium iridium and ruthenium chlorides, is ignited, and the residual metals are fused for two hours in a silver basin with a mixture of two parts potassium nitrate and one part potassium carbonate, and dissolved in water, leaving the bluish potassium iridate. The solution is treated with nitric acid until the yellowish-red color, due to the presence of potassium rutheniate, disappears, and the ruthenium is precipitated as oxide, which is ignited in a graphite crucible and fused by means of the oxyhydrogen flame or in the electric furnace.

DETECTION.—Boil the solution, supposed to contain ruthenium, with a little hydrochloric acid, then neutralize by adding ammonia, add a solution of sodium thiosulphate, mixed with ammonia, and boil the mixture. If ruthenium is present, a purple-red liquid is produced, which, unless the solution is very dilute, appears black by transmitted light. This coloration is permanent, and the liquid may be exposed to the air without alteration.

Or, render the solution to be tested for ruthenium alkaline by the addition of sodium or potassium carbonate, and then add potassium nitrate in solution. Boil the mixture for an instant, allow it to become perfectly cool, and add a drop or two of colorless ammonium sulphide. On shaking, a yellow or orange-yellow color appears, which quickly deepens to the finest red. When the quantity of ruthenium present is very small, or when large quantities of the other platinum metals are also present, it is better, after adding the alkaline carbonate and nitrate, to evaporate the whole to perfect dryness on the water bath, and treat the dry and powdered mass with a small quantity of absolute alcohol. The alcoholic solution is then filtered off and treated directly with ammonium sulphide. In this manner the smallest trace of ruthenium may be detected even in the presence of very large quantities of the other platinum metals.

QUALITATIVE DETERMINATION.—Hydrogen sulphide produces at first no precipitate, but after some time the fluid acquires an azure-blue tint, and deposits brown ruthenic sulphide, Ru_2S_3. This reaction is very delicate and characteristic.

Ammonium sulphide produces a brownish-black precipitate, difficultly soluble in excess.

Potassium hydrate precipitates black ruthenic hydrate, $Ru_2(OH)_6$, insoluble in alkalies, but soluble in acids.

Potassium sulphocyanate produces, in the absence of other platinum metals, after some time, a red coloration, which gradually changes to purple-red, and, upon heating, to a fine violet tint. (Very characteristic.)

Potassium chloride or ammonium chloride produce in concentrated solutions crystalline glossy violet precipitates of the double chlorides, difficultly soluble in water, insoluble in alcohol. They are decomposed on boiling with water, with separation of black ruthenious oxychloride.

Potassium nitrite forms a double salt, $3NOKO, N_2O_3, RuO_3$, readily soluble in an excess of the alkaline nitrite. On the addition of a few drops of colorless ammonium sulphide, the solution assumes a splendid dark red color, changing to brown, without precipitation of sulphide.

Metallic zinc produces at first a fine azure-blue coloration (owing to the reduction of Ru_2Cl_6 to

$RuCl_2$), which subsequently disappears, ruthenium being deposited in the metallic state.

QUANTITATIVE ESTIMATION.—This operation is effected according to the directions given under "Chemistry and Commercial Points."

CHAPTER XII.

IRIDIUM.

CHEMISTRY AND COMMERCIAL POINTS.—The production of the metal was described under the caption "Osmium." Iridium is a white, steel-like metal of atomic weight 192.5, and specific gravity 22.42, which fuses at 1950° C. It is brittle when cold, and somewhat malleable at a white heat. At a red heat it is superficially oxidized, but becomes reduced again at 1000° C. When pure, it is insoluble in aqua regia, but when alloyed with much platinum, it dissolves in that liquid. Iridium occurs in platinum ore, principally as osmiridium and platiniridium, the former remaining behind after the treatment with aqua regia. When osmiridium is fused with zinc and some ammonium chloride, the two metals contained in it unite, and when the fusion is completed the zinc may be dissolved from the cooled mass by means of dilute sulphuric acid, when iridium and osmium remain as impalpable powders.

When a solution of iridium sulphate, containing alcohol, is exposed to sunlight, the metal separates from the liquid in form of a fine iron-black powder, which is more energetic in its action than platinum black. If this powder is washed and dried, and a small portion of it is placed upon a paper saturated with alcohol, the paper will take fire and burn. The metal itself, when held in the flame of an alcohol lamp, absorbs carbon, forms an iridium carbide, and covers itself with black excrescences containing much iridium, which ignite on exposure to the air.

Osmiridium, as well as metallic iridium, is used to a considerable extent for manufacturing purposes. Thus the native alloy serves on account of its extreme hardness, infusibility and indifference to reagents, for watch and compass bearings and the pointing of pens, while iridium itself is used for the construction of knife edges, of delicate balances and other hard-wearing surfaces. Of the native osmiridium only ten per cent., however, is available for pen points, as it occurs mostly in very small grains, one ounce of the mineral containing between three to six thousand of them, many of them being too small for use, and others breaking when being worked on account of their laminated structure. On manufacturing these pen tips, a suitable grain is selected, and attached to the end of the pen with ordinary silver solder, cut through to form two halves of the nib by means of a revolving copper-plate tipped with diamond dust, and ground to the required shape on a revolving copper-plate with emery and oil. In this manner about thirty ounces of osmiridium are used annually in the United States. The principal district which furnishes most of the native alloy is Katharinenberg in the Urals, since the yearly production amounts there to about two hundred ounces. Other parts of these mountains contribute to the output in a small degree. The California mineral, which contains less platinum, and is heavier, denser and harder than that of the Russian districts, is best suited for general purposes and much preferred in consequence.

The prices of platinum metals by the gram are: Iridium, metallic, $1.07; in grains, 50 cents. Osmium, $2. Palladium, sheet and wire, $1.50; powder, 80 cents. Rhodium, $3.25. Ruthenium, $1.60.

DETECTION.—On dissolving platinum ore in aqua regia, the osmiridium remains almost untouched. To distinguish iridium, mix the mineral supposed to contain that metal, intimately with sodium chloride, place the mixture in a porcelain boat, heat the mass in a current of chlorine, and dissolve the double chloride of iridium remaining in the boat in water. Iridium, thus treated, yields a black-brown solution, rhodium a rose-red, and ruthenium an orange-yellow liquid. Evaporate the solution on the water bath, place it in a porcelain boat and reduce the residue to the metallic state by ignition in a current of hydrogen. It will be seen that the presence of both iridium and osmium can be traced simultaneously by the process described.

QUALITATIVE DETERMINATION.—Hydrogen sulphide first decolorizes the solution of an iridium salt with separation of sulphur and reduction of the

$IrCl_4$ to Ir_2Cl_6, and finally precipitates brown iridic sulphide, Ir_2S_3.

Ammonium sulphide produces the same precipitate, which is readily soluble in excess.

Potassium or sodium hydrates, added in excess, color the solution greenish, and precipitate a little brownish-black iridium potassium or sodium chloride. On heating the liquid with exposure to the air, it acquires at first a reddish tint, which changes afterwards to azure-blue (distinction from platinum), and when evaporated to dryness and taken up with water, a colorless solution is obtained, and a blue deposit of iridic dioxide is left undissolved.

Potassium chloride precipitates dark brown potassium iridium chloride of the formula $IrCl_4$ 2KCl, insoluble in a concentrated solution of potassium chloride.

Ammonium chloride throws down from concentrated solution a dark red powder, consisting of small octahedral crystals of iridium ammonium chloride of the composition $IrCl_4\ 2NH_4Cl$, which is insoluble in a concentrated solution of the precipitant.

Reducing agents, such as potassium nitrite, oxalic acid, ferrous sulphate, stannous chloride and mercurous nitrate, reduce the double salt of ammonium as well as the potassium double chloride, especially when in hot solutions, to the sesqui-salt, thus:

$2(2KCl\ IrCl_4)+4KNO_2=6KCl\ Ir_2Cl_6+2KNO_3+2NO.$

The double chloride crystallizes out on cooling.

When iridium hydrate of the formula $Ir(OH)_4$, is suspended in a solution of potassium nitrite, and the solution saturated with sulphurous acid and boiled, with renewal of the water, as long as sulphur dioxide is given off, the whole of the iridium is converted into insoluble brownish-green iridium sulphite of the composition $(IrO)SO_4$ $4H_2O$. This reaction serves also for the separation of iridium from platinum.

Metallic zinc precipitates black metallic iridium.

Iridium salts are reduced by alcohol in alkaline solutions to insoluble iridious compounds.

QUANTITATIVE ESTIMATION. — The quantitative estimation of iridium is accomplished according to the directions given under "Detection."

CHAPTER XIII.

SELENIUM.

HISTORY.—Selenium was discovered in 1817 by the renowned Swedish chemist Berzelius in the flue dust of the lead chambers of the sulphuric acid works at Gripsholm, Sweden, where sulphur, produced by roasting iron pyrites from Fahlum, was used for manufacturing the acid. The dust, when tested before the blowpipe, gave off a penetrating smell resembling that of rotting horseradish, which behavior was considered at that time as characteristic of the presence of tellurium. A more careful investigation, made by Berzelius, showed, however, that an unknown element was present, which was called by him selenium from the Greek noun "selene," meaning moon. The reason underlying the choice of this name consisted in the circumstance that the properties of selenium approached strikingly those of tellurium, which term is derived from "tellus," the Latin word for earth, and since the earth and moon are in close proximity, comparatively speaking, Berzelius selected that name. In connection with this occurrence it will be noticed that the appellations of several chemical elements like palladium, tellurium, uranium and selenium, discovered in earlier years, were derived with predilection for the names of astral bodies—a propensity which came to the discoverers as an inheritance from the alchemists, who imagined the chemical compounds which they handled to be affected by a mysterious influence exerted upon them by the stellar system.

CHEMISTRY AND COMMERCIAL POINTS.—This element, of the atomic weight 79.1, approaches sulphur in its properties, and forms, like the latter, several allotropic modifications, distinguished as the amorphous and crystalline varieties. Amorphous selenium, obtained by the reduction of the dioxide SeO_2 by means of sulphur dioxide, is a reddish-brown powder, soluble in carbon disulphide, and has a specific gravity of 4.26, while the crystalline variety results on heating amorphous selenium to 97° C., when the temperature of the mass rises suddenly above 200° C., and the selenium is converted, on allowing it to cool slowly, into a crystalline, dark-gray substance of specific gravity 4.8. This modification possesses metallic lustre, conducts electricity, and is insoluble in carbon disulphide. Its resistance increases when heated, but diminishes considerably on exposure to light, and returns after removing it from the latter. The change in conductivity is instantaneous, even the light produced by a small lamp having a noticeable effect, while it is almost doubled in sunlight. On this property is based the construction of an instrument, known as photophone, in which light is converted into electricity, and sounds and even articulate speech can be transmitted from a distance.

Selenium has also been recently used for observations, made during the transit of Venus, and the occurrence of the sun's eclipse. The element melts at 217° C., boils at about 700° C., and passes then into a dark yellow vapor. It dissolves with a green color in concentrated sulphuric acid, and forms then selenious acid.

Seleniferous flue dust accumulates in the conduits leading from the burners to the lead chambers of sulphuric acid factories, using seleniferous pyrites, and consists of a mixture of selenium and metallic selenides with soot and sand. This material serves for the preparation of selenium. It contains in cases thirty to forty per cent. of the metal, and forms a dark colored mass, which is first moistened with sulphuric acid, then washed with water and thoroughly dried, to be finally placed into a luted glass retort. The latter is then strongly heated to a temperature approaching the fusing point of glass, when most of the selenium distils over in perfectly pure condition. The residue, consisting of selenides with carbon and other impurities, is dissolved in hydrochloric acid containing a little nitric acid, and the iron and copper present are precipitated with caustic soda. The mixture is then filtered, and the selenium contained in the filtrate recovered by saturating the liquid with sulphur dioxide.

Selenium counts, however, with the rare metals, and is but difficultly obtained in large quantities. Chemically pure and crystallized selenium can be bought at $1 per gram, and the commercial article for ten cents per gram.

MINERALOGY.—Selenium occurs native in the cavities of Vesuvian lavas, and as sulphur selenide in natural sulphur, also in several varieties of copper and iron pyrites, especially in those of Norway, and in meteoric iron. In the Hartz mountains, Germany, are found the rare minerals clausthalite PbSe, lehrbachite PbSe HgSe, onofrite HgSe 4HgS, eucairite $CuSeAg_2Se$, and crookesite(CuTlAg)Se, which are, however, not met with in the United States.

DETECTION.—Dissolve the ore supposed to contain selenium in concentrated nitric acid, add a few drops of hydrochloric acid, and boil. Add barium chloride to remove any sulphur, eventually present as sulphuric acid, filter, dry, and weigh the barium sulphate formed, and reduce the selenium in the filtrate by means of sulphur dioxide. It will be seen that this process is also applicable for the detection and estimation of sulphur in seleniferous ores. In most cases selenium may be separated from metals by heating the ore containing it in a current of chlorine. The selenium chlorides thus formed are sufficiently volatile to render the separation easy of execution.

QUALITATIVE DETERMINATION.—Hydrochloric acid decomposes selenates on boiling; chlorine is evolved, and the salt is reduced to a selenite. (Distinction from SeO_2.) Hydrogen sulphide does not produce a precipitate until the selenate has been reduced to selenite by boiling with hydrochloric acid. Barium chloride produces a white precipitate of barium selenate, $BaSeO_4$, insoluble in water and in dilute acids; decomposed by boiling hydrochloric acid.

Selenious compounds, when treated with hydrogen sulphide, produce from an acid solution of a selenite a lemon-yellow precipitate of selenious sulphide SeS_2, which almost immediately breaks up into its component elements Se and S_2, but is readily soluble in ammonium sulphide. Barium chloride gives a white precipitate of barium selenite, $BaSeO_3$, soluble in dilute hydrochloric or nitric acid. Reducing agents, such as SO_2, alkaline sulphite, stannous chloride, metallic zinc and iron, precipitate from solutions, acidulated with hydrochloric acid, metallic selenium, as a red powder, which turns gray at a high temperature and is soluble in potassium cyanide solution. Ferrous sulphate is without-action. Metallic copper is immediately coated black, when placed in a warm solution containing hydrochloric acid, and on standing, the solution turns light red from separation of metallic selenium.

QUANTITATIVE ESTIMATION.—As selenium and tellurium occur as a rule together, provision is to be made for the separation of both elements. Treat one gram of the seleniferous ore with aqua regia, and precipitate the gold, frequently present in the solution, by means of oxalic acid. Filter off the gold, conduct sulphur dioxide through the liquid to precipitate selenium and tellurium and dilute with water to render the precipitation complete. Dissolve the precipitate in nitric acid, filter off the tellurous acid, and distil the filtrate containing the selenium.

Or, heat one gram of the finely powdered ore with a solution of potassium cyanide on the water bath for eight hours, and collect the precipitated tellurium on a tared filter. Add hydrochloric acid to the filtrate to throw down the selenium, filter it off, mix the filtrate with sodium sulphite solution, heat and allow to stand for twenty-four hours. The proportion of tellurium, which has been dissolved as potassium tellurate, is thus completely precipitated. Collect the precipitate by filtering through the first filter used for gathering the tellurium, dry over the water bath and weigh. Treat the precipitated selenium in the same manner.

If iron, copper or other metals are present, which form soluble compounds with the reagent, partly precipitated by hydrochloric acid, eliminate them by dissolving the ore in acid, and add to the solution sufficient ammonium sulphide to dissolve the tellurium and selenium. Add hydrochloric acid to the solution, until complete precipitation is effected, and treat the precipitated sulphides with potassium cyanide as described above.

CHAPTER XIV.

GERMANIUM.

History and Mineralogy.—Germanium, thus called from the Latin name Germania, was discovered in 1886 by the distinguished chemist Clemens Winkler in a rare mineral, called argyrodite, which is found in the Himmelsfuerst mine near Freiberg, Germany, and forms steel-gray monoclinic crystals of metallic luster, having the specific gravity 6.093. This mineral occurs also in form of a thin coating of pyrites or of argentite—a silver sulphide of the formula Ag_2S—and carries then germanium to the extent of only 0.03 per cent. After repeated analyses of argyrodite to the number of eight, which regularly differed by seven per cent., Winkler came to the conclusion, that the discrepancy thus occurring must be due to the presence of some unknown element. Following this train of thought he succeeded by subsequent careful researches in isolating the metal, and in ascertaining the nature of its compounds. Finally he established the following composition of the mineral as the correct one:

Ag	74.72
Ge	6.93
S	17.13
FeO	0.66
ZnO	0.22
Hg	0.31
Total	99.97

These figures correspond to the formula $3Ag_2S GeS_2$ not considering the small admixtures of iron, zinc and mercury, contained in the ore. Subsequently it was found that the mineral euxenite, a niobate and tantalate of yttrium, uranium, erbium and cerium, also contained as a rule one-tenth per cent of germanium.

A remarkable circumstance, connected with the discovery of the new element, was the fact that the Russian chemist Mendelejeff had predicted its existence as early as 1871. He stated at that time in a treatise, since become famous, and referring to the relations existing between the properties of the elements and their atomic weights, as follows: "The ekasilicon (later named germanium by Winkler) forming the oxide EsO_2, takes a position in the periodic system of the elements, intermediate between ekaaluminum (now gallium, also predicted by Mendelejeff), and arsenic on the one hand, and on the other between silicon and tin. Its atomic weight will be found to be about 72, its specific gravity 5.5, and that of the oxide 4.7. The chloride of ekasilicon will be a volatile liquid, boiling at 100° C. or probably a little lower, and will possess a specific gravity of 1.9. The ethyl compound of ekasilicon will boil at 160° C., and have a density of about 0.96."

In accordance with this prediction, the atomic weight of germanium was found fifteen years later to be 72.32, its specific gravity 5.469, that of germanium oxide 4.703, the boiling point of germanic chloride 86, that of germanium ethyl as 160° C., and the specific gravity of the chloride as 1.887.

Germanium belongs, therefore, to the fourth group of the periodic system of the elements, that is to the same series of which carbon and silicon are the first members, so that the main group may be represented as follows:

Carbon of the atomic weight...	12
Silicon of the atomic weight...	28.4
Germanium of the atomic weight	72.3
Tin of the atomic weight......	118.1
Lead of the atomic weight.....	206.91

This constellation showed that the discovery of an element whose atomic weight would lie between those of tin and lead, and approached the figure 160, was yet to be accomplished, and this expectation was fulfilled in later years by the discovery of the metal erbium, of the atomic weight 166.

CHEMISTRY AND COMMERCIAL POINTS.—Metallic germanium of atomic weight 72.3 and specific gravity 5.469, is a brittle, silver-white substance, resembling tin in its physical properties and chemical behavior.

It is very stable in the air, but burns, when heated in the gas flame, giving off white vapors, which condense on cooling to the dioxide GeO_2. The metal melts at 900° C., and crystallizes readily, on solidifying, into beautiful, grayish-white, metallic octahedra. It is insoluble in hydrochloric acid, and is converted by nitric acid into the hydrated dioxide.

The production of the metal includes the preparation of the dioxide from sodium sulpho-germanate, which is obtained by fusing the germaniferous mineral with sulphur and soda, and extracting the sodium salt with water. The solution thus obtained, is treated with hydrochloric or sulphuric acid, when the sulphide, GeS_2, separates out in form of a white voluminous precipitate, which is insoluble in acids, but soluble in water. The sulphide thus produced is then either roasted or treated with nitric acid, when the dioxide results, which is reduced to the metallic state in a current of hydrogen, or fused with powdered charcoal in a wind furnace to obtain the metal. The price of this rare metal is quoted at $75 per gram, when in the molten state, and at $70 when in the form of powder.

DETECTION.—Fuse the ore to be tested for germanium with sulphur and soda, dissolve the fusion in water, filter and add a few drops of hydrochloric acid to the filtrate containing the sulpho-salt. Filter off the white germanic disulphide thus precipitated, wash with strongly acidulated water, and heat the residue in a current of hydrogen, to reduce the disulphide to germanous sulphide, GeS, which is thus obtained in grayish-black crystals. Dissolve the latter in hot hydrochloric acid, to form the dichloride $GeCl_2$, and conduct hydrogen sulphide through the solution to precipitate the characteristically colored reddish-brown germanous sulphide.

QUALITATIVE DETERMINATION.—Hydrogen sulphide precipitates from solutions of germanous salts the reddish-brown germanous sulphide, soluble in hot hydrochloric acid, but from germanic solutions the white voluminous germanic sulphide, GeS_2. The latter is insoluble in acids, but readily soluble in water. (Characteristic reaction.) It is reprecipitated by the addition of acids, and especially on conducting a current of hydrogen sulphide through them. Germanic sulphide dissolves readily in the fixed alkaline hydrates and in ammonia, forming sulpho-salts, which are perfectly analogous to the corresponding sulpho-stannates. Caustic alkalies precipitate germanous hydroxide $Ge(OH)_2$ as a yellow colored compound from germanous solutions. It is soluble in hydrochloric acid. When adding solutions of alkalies to a germanic salt, the white germanic hydroxide $Ge(OH)_4$ or $GeO(OH)_2$ separates out, which is soluble in the hydrates and carbonates of the alkalies, but insoluble in acids. Germanium chloroform of the formula $GeHCl_3$, analogous to ordinary chloroform $CHCl_3$, is produced when metallic germanium is heated in a current of hydrochloric acid gas. It is a mobile liquid, boiling at 72° it becomes cloudy on exposure to air, and gradually colorless, oily drops of germanium oxychloride of the formula $GeOCl_2$ separate out.

Quantitative Estimation.—This operation coincides with the directions given under "Chemistry and Commercial Points" and "Detection."

CHAPTER XV.

URANIUM.

HISTORY.—In the year 1789 the German chemist Klaproth recognized in specimens of pitchblende the presence of an unknown metal, which he called uranium, from the planet Uranus. The ores tested by him were found near Johanngeorgenstadt in the mountain chain of Saxony, known as Erzgebirge (ore mountains), and at Joachimsthal (Joachim's valley) in the Bohemian division of those mountains, which have furnished considerable uranium ore unto the present time. Subsequently the distinguished chemist Berzelius and many other prominent men of the profession investigated the properties of the metal and its compounds more closely and in 1840 the French chemist Peligot succeeded in isolating metallic uranium from the chloride.

CHEMISTRY AND COMMERCIAL POINTS.—Metallic uranium of atomic weight 239.4 and specific gravity 18.7 has a steel-gray color, resembling that of nickel. Its melting point lies near 1500° C., and its hardness surpasses slightly that of wrought iron. It changes into uranous-uranic oxide when heated in the air. The metal or its carbide has the peculiar capability of imparting desirable properties to iron or steel, when fused with the latter in low percentages, and for this reason it ranks prominently with other metals of this class, as chromium, nickel, molybdenum, tungsten and vanadium. It is said to improve the toughness, hardness and elongation of steel and iron to a remarkable extent, when applied in the manner indicated, so that the alloy has been employed for the preparation of a superior gun metal, serving for the casting of heavy ordnance and armor plate. In connection with this observation it is remarkable to note that the addition of nickel to steel was primarily caused by the study of the composition of meteorites, which contain besides prevailing quantities of iron, small percentages of nickel. They are known for their extreme hardness and toughness, and hence gave the first incentive for experiments in that line.

Furthermore uranium oxide possesses the property of imparting to glass a beautiful fluorescence of a greenish-yellow hue, and a fine velvety-black to porcelain, when heated in the enameling. It also finds application in the manufacture of Welsbach mantles, as it is considered a welcome addition in cases to the thorium, cerium and zirconium salts applied for that purpose. Uranium salts have been found lately to emit a light. resembling phosphoresence, which has the property of passing through thin sheets of aluminum and cardboard of considerable thickness. This light partakes, therefore, of the qualities of the X-rays, and if a piece of pitchblende is placed on a sensitized plate in a dark room a photograph of the mineral will be produced in the course of time.

The manufacture of uranium compounds, as uranium oxide or sodium uranate, is naturally limited to the treatment of pitchblende and that of carnotite, since these two minerals alone occur in commercial quanitites. In the first case the ore is to be freed of impurities, which consist mainly of sulphur, arsenic, lead and iron. To achieve this purpose the pitchblende is reduced to a fine powder, separated from the lighter earthy admixtures, roasted for a short time to remove part of the sulphur and arsenic, then dissolved in nitric acid, and the solution evaporated to dryness. The residue is exhausted with water, and the solution filtered from a brick-red residue of ferric oxide, ferric arsenate, and lead sulphate. On evaporating, the aqueous solution yields crystals of the nitrate, which may be obtained in pure condition by dissolving them in ether, and allowing the latter to vaporize. A subsequent recrystallization can be effected furthermore by dissolving the salt in boiling water, when pure uranyl nitrate of the formula $UO_2(NO_3)_2+6H_2O$ will separate out.

In the case of carnotite, the treatment consists primarily in a washing of the ore with water, so as to eliminate especially clayey matter, whose presence would interfere with the percolation of the sulphuric acid to be applied afterwards. The contents of uranium oxide in the ore having been determined beforehand a small excess of sulphuric acid and water is added, sufficient to decompose the mineral completely, and the mixture heated, until the residue consists of nothing else but sandy matter. To ascertain this point an examination of the residue by means of a magnifying glass is advisable.

When manufacturing on a large scale the washed ore is placed in a vat, heated by means of a coiled lead pipe, through which steam circulates, when the water and acid are added, and the mixture is heated to boiling. As soon as complete decomposition has been effected a considerable excess of sodium carbonate, approximately calculated beforehand, is added, also additional water if necessary, and the steam turned on again. The addition of sodium carbonate in excess is made in order to bring the uranium values into solution. The boiling of the mixture is then continued for about fifteen minutes—all these operations being performed in the same vat—and the yellowish solution thus resulting allowed to settle and clear. It is then siphoned into a precipitating vat, and thus separated from the pasty residue, containing mainly carbonates and hydrates of the earthy compounds present, when the yellow sodium uranate is thrown down from the now practically pure solution by means of caustic soda. As the salt thus obtained is nearly insoluble in water, it is washed with the latter on cloth filters, or treated in a filter press to deprive it of its wash water. This precipitation by means of caustic soda can also be applied to the solution of uranyl nitrate, obtained by the treatment of pitchblende, in case it is intended to manufacture sodium uranate, which is a commercial article. If the process described above is properly conducted the final product obtained contains nearly 76 per cent. of the oxide U_3O_8.

The pasty residue mentioned above, which contains much silica, alumina, lime and magnesia and small amounts of iron, serves for the preparation of artificial fullers' earth. It is mixed and ground for that purpose, while moist, in the proportion of four parts of the precipitate to five of the sand, and the mixture heated to dryness, when a substance results which has all the properties of fullers' earth.

It has been found advantageous to treat the ore in place and to ship the concentrates, since the high freight charges to New York, which is the usual shipping point, are too high to allow of railroad transportation for low grade ore. High grade ore is but rarely met with and hence shipments of this kind have been very limited. Chemically pure metallic uranium sells at $2 per gram and this price refers to the fused article only. The oxide brings between $1.25 and $1.60 per pound according to the percentage contained in the ore, as becomes evident from the following table:

Ores of	10 per cent U_3O_8	$1.25 per lb. of oxide present
Ores of	15 per cent. U_3O_8	1.39 per lb. of oxide present
Ores of	20 per cent. U_3O_8	1.45 per lb. of oxide present
Ores of	25 per cent. U_3O_8	1.55 per lb. of oxide present
Ores of	30 per cent. U_3O_8	1.60 per lb. of oxide present

and higher in proportion. A 10 per cent. uranium ore would bring, therefore, $250 per ton of 2,000 pounds. Pitchblende is valued in the same manner, that is according to its contents in uranium oxide.

MINERALOGY.—A great number of uranium bearing minerals occur in nature, but those of commercial importance are limited to two, namely uranite or pitchblende, and carnotite, both of which occur in available quantities only in the state of Colorado. These two minerals alone will, therefore, find consideration in the following lines.

Pitchblende, the naturally occurring compound of uranous and uranic oxide, corresponding, when in pure condition, to the formula $UO_2\ 2UO_3 = U_3O_8$, is found in the Wood mine, German lode, and Kirk mine of Gilpin county, Colorado, in pockety formation, and associated with a large number of foreign bodies, the most prominent of which are iron and copper pyrites. The mineral is also known to occur in the Bald mountain district of the Black Hills, South Dakota, but only in very limited amounts of low percentage. Pitchblende occurs as a rule in massive form, but is occasionally found in the crystallized condition when it forms dark brown translucent crystals. Its fracture is conchoidal to uneven, its hardness 5.5, and its specific gravity varies between 8 and 9.7, so that it may be readily recognized by its extraordinary heft. It occurs frequently, however, in altered form, that is partly or entirely changed by the effects of the atmosphere and moisture into the yellow hydrated oxide.

whereby its specific gravity becomes lowered, and its color varied into canary-yellow or a somewhat darker reddish shade. Uraninite, when pure, is opaque, of a velvety-black to grayish appearance, has a submetallic, greasy or pitch-like, dull lustre, and gives a streak verging from brownish-black to grayish and olive-green. The variety from Colorado has a specific gravity of 8.07, is compact and usually associated with iron pyrites. It contains, like most of the uraninites, a certain percentage of the rare gaseous element argon, which was mistaken for nitrogen when first discovered, and is now known to be present also in slight amounts in the atmosphere. The following analytical data will make these points more clear:

Uraninite from Colorado.	
U_3O_8	83.71 per cent.
ZrO_2	7.59 per cent.
CeO_2	0.22 per cent.
PbO	0.70 per cent.
CaO	0.84 per cent.
ZnO	4.72 per cent.
Argon	0.15 per cent.
H_2O	1.96 per cent.
	99.89

Uraninite from Joachimsthal.	
U_3O_8	76.0 per cent.
S	0.6 per cent.
FeO	3.1 per cent.
Pb	4.2 per cent.
CaO	5.2 per cent.
MgO	2.0 per cent.
CO_2	3.3 per cent.
SiO_2	3.5 per cent.
H_2O	1.3 per cent.
	99.2

Pitchblende is also known to occur, besides the localities mentioned, in the Cornwall mines of England, associated with numerous other minerals, but the productivity of these mines is said to be rather limited in recent years.

The second uranium mineral of importance is carnotite, thus called from the French scientist Carnot, which is essentially a uranyl potassium vanadate, contaminated with calcium and barium compounds, and a mixture of silicates containing vanadium. The pure mineral constitutes a loosely cohering mass of yellow color, which leaves traces whenever touched or placed. Deposits of carnotite occur in Montrose, San Miguel, Dolores and Montezuma counties, Colorado, those of Montezuma having been discovered recently. Further extensions of the ore bodies have been traced across the boundary line into Utah near Moab, but these are of very low grade and of little significance. The entire productive area comprises a territory of about a hundred square miles, and may be divided into four districts, namely those of La Sal creek, Roc creek, Hydraulic and McIntyre canon. The ore obtained at La Sal creek is characterized by the presence of molybdenum compounds, that of Roc Creek by its copper contents, the mineral from Hydraulic by its percentages in lime, and that of Placerville by the presence of roscoelite—a vanadium mica, in which the values in vanadium pentoxide range upward to twenty-nine per cent. Carnotite is usually found disseminated through sandstone in flat-lying streaks of a few inches thickness, which frequently disappear when followed into the hillside. Occasionally pockety formations are encountered in these layers, which contain the high grade ore carrying in cases up to fifty-five per cent. of uranium oxide, but the greater portion of the deposits contain as a rule only a percentage of that compound varying between two and four. The composition of the mineral is as follows:

Carnotite from Roc Creek.		Carnotite from La Sal Creek.	
	Per Cent.		Per Cent.
Insoluble residue	7.10	Insoluble residue	10.33
UO_3	54.89	UO_3	54.00
V_2O_5	18.49	V_2O_5	18.05
P_2O_5	0.80	P_2O_5	0.05
As_2O_5	Trace	As_2O_5	None
Al_2O_3	0.09	Al_2O_3	0.29
Fe_2O_3	0.21	Fe_2O_3	0.42
CaO	3.34	CaO	1.86
SrO	0.02	SrO	Trace
BaO	0.90	BaO	2.83
MgO	0.22	MgO	0.14
K_2O	6.52	K_2O	5.46
Na_2O	0.14	Na_2O	0.13
Li_2O	Trace	Li_2O	Trace
H_2O 105° C.	2.43	H_2O 105° C.	3.16
H_2O 350° C.	2.11	H_2O 350° C.	2.21
H_2O+350° C.	None	H_2O+350° C.	None
PbO	0.13	PbO	0.07
CuO	0.15	CuO	Trace
SO_3	None	SO_3	None
MoO_3, 0.18; SiO_2, 0.15; TiO_2, 0.03; CO_2, 0.56=98.46.		MoO_3	0.05
		SiO_2	0.20
		TiO_2, CO_2, none=99.25.	

Detection.—Borax and microcosmic salt give with uranium compounds in the inner flame of the blowpipe green beads, in the outer flame yellow beads, which acquire a yellowish-green tint on cooling. The oxides of uranium are not reduced by fusion with sodium carbonate on charcoal.

QUALITATIVE DETERMINATION.—Uranous salts are powerful reducing agents. They are green, or greenish-white, and yield green aqueous solutions.

$(NH_4)_2S$ forms a black precipitate of uranous sulphide, US.

NH_4OH, KOH or NaOH throw down red-brown gelatinous uranous hydrate, $U(OH)_4$.

K_2CO_3, Na_2CO_3 or $(NH_4)_2CO_3$ precipitate green uranous hydrate, soluble in excess, especially in excess of $(NH_4)_2CO_3$.

Uranous salts become oxidized to uranic salts by exposure to air, or by treatment with nitric acid or other oxidizing agents. Gold and silver salts are speedily reduced by them, and ferric salts are reduced to the ferrous state.

Uranic salts are yellow, mostly soluble in water, and are reduced to uranous salts by H_2S, alcohol, ether and sunlight.

$(NH_4)_2S$ produces in the cold a chocolate-brown precipitate of uranyl sulphide, containing also ammonium sulphide and water. It is insoluble in yellow ammonium sulphide. On warming or boiling the liquid containing the uranyl sulphide $(UO_2)S$, the precipitate splits up into sulphur and black uranous oxide, UO, which is insoluble in excess of $(NH_4)_2S$.

Uranyl sulphide dissolves readily in neutral ammonium carbonate. (Method for separating U from Zn, Mn and Fe.)

NH_4OH, KOH or NaOH produce a yellow precipitate, consisting of acid uranate of the alkali metal, which is insoluble in excess of the precipitant, and is not precipitated in the presence of tartaric acid.

The ammonium precipitate is soluble in a solution of ammonium carbonate, and ammonium sulphide does not precipitate the uranium from this solution.

K_2CO_3, Na_2CO_3 or $(NH_4)_2CO_3$ give a light yellow precipitate, consisting in the case of potassium carbonate of potassium uranic carbonate, readily soluble in an excess of the precipitant. By treating the liquid with dilute sulphuric acid, as long as effervescence takes place, an acid uranate is preciptated. (Method of separating U from Al and Fe.)

$BaCO_3$ completely precipitates a solution of a uranic salt, even in the cold. (Separation of U from Ni, Co, Mn, Fe and Zn.)

K_4FeCy_6 produces a reddish-brown precipitate. (Most delicate special reaction.)

Metallic zinc does not precipitate metallic uranium from its solutions.

Quantitative Estimation.—Dissolve one gram of the finely pulverized ore supposed to contain uranium values in five cubic centimeters of nitric acid and add a little water, and heat. If complete decomposition cannot be effected in this manner, add five cubic centimeters of sulphuric acid and heat until the ore is entirely decomposed. Take up with water, and without filtering, supersaturate the solution with sodium carbonate. Boil for about ten minutes, when the complete solution of the uranium compound in the excess of sodium carbonate will have taken place. Filter to remove the metallic carbonates and alumina precipitated, and add to the clear filtrate a concentrated solution of caustic potash, to throw down the uranium as potassium uranate, which has a deep yellow color, and is insoluble in water. Filter, dissolve the precipitate on the filter in dilute nitric acid, oversaturate the solution thus obtained again with sodium carbonate, and boil to remove the small amount of ferric iron, which is always carried down during the first precipitation. Repeat the latter, employing caustic potash, filter, wash, dissolve the potassium uranate on the filter in dilute nitric acid, and throw down the yellow ammonium salt from the solution by means of ammonia in excess. Filter off the precipitate, wash, incinerate and glow in an open crucible, cool and weigh the green oxide $U_3O_8=UO_2\ 2UO_3$ of the molecular weight 846.2, and calculate from the weight of the latter the percentage of uranium values present.

In case the mineral to be analyzed contains copper, it is better to remove that metal first from the acid solution of the mineral by saturating it with hydrogen sulphide, to filter off the sulphide precipitated, and to heat the filtrate under the addition of a few drops of nitric acid and a little potassium chlorate, to oxidize it, when the liquid is treated with excess of sodium carbonate, as described above.

Should arsenic acid be present in the solution obtained by dissolving the mineral in acid, it is advisable to reduce that compound to arsenious acid by adding sulphurous acid to the liquid and heating. If then, after cooling, a current of hydrogen sulphide is conducted through the solution, the arsenic is immediately precipitated by the gas.

(See Appendix.)

CHAPTER XVI.

INDIUM.

History.—Indium belongs to a series of metals whose existence was ascertained by spectrum analysis. It was discovered by means of the spectroscope in 1863 by Reich and Richter on examining zincblende from Freiberg. The ore employed by them consisted chiefly of blende, galena and arsenical pyrites, and was first roasted to expel sulphur and arsenic, when it was treated with hydrochloric acid, and the resulting solution evaporated to dryness. The impure chloride thus obtained, exhibited, when examined by the spectroscope, only one indigo-colored line, but when it had been purified and the hydrate and the metal itself been prepared, and then subjected to spectrum analysis, the first observed line was seen in great brilliancy, and with it appeared a second fainter blue line. Consequently the metal received its name from these two indigo-blue lines, which are characteristic of the indium spectrum.

Chemistry and Commercial Points.—Indium of atomic weight 113.4 and specific gravity 7.42 is a silver-white metal, devoid of crystalline structure, resembling platinum in appearance. It is easily malleable, since it is softer than lead, and marks paper most readily. Its melting point lies at 176° C., but it is nevertheless less volatile than zinc or cadmium, whose melting points are 335° C. and 320° C. respectively. Indium retains its lustre, when exposed to the effect of the air or boiling water, imparts a violet tint to an incandescent gas flame, and oxidizes before the blowpipe, coloring the flame blue. It dissolves slowly in hydrochloric and sulphuric acids, but readily in nitric acid. Chemically indium belongs to the earth-metals, of which aluminum is the characteristic element, forming an alum of the formula $In_2 (SO_4)_3 (NH_4)_2SO_4+24 H_2O$ with ammonium, but not so with sodium or potassium. It is easily reduced from its oxide In_2O_3 by heating the latter in a current of hydrogen, and is precipitated from solutions by cadmium and zinc. Metallic indium may be bought from Messrs. Eimer & Amend, New York, at $5.50 per gram, the high figure demanded for the metal being caused by its extraordinary scarcity.

Indium does not occur native, but is found in minute quantities in zincblende, notably in that from Freiberg, Germany, also in the calamine from Onela in the province of Bergamo, Italy, which is said to be rich in indium, comparatively speaking. It is best prepared, however, from the spelter of indiferous blendes, which is treated with a quantity of hydrochloric acid not sufficient to dissolve it entirely, when the residue thus obtained will contain all the indium originally present.

The zinc from the Freiberg mines contains, besides a small amount of lead, iron, arsenic and cadmium, 0.0448 per cent. of indium. To separate the latter, the zinc is dissolved in dilute sulphuric or hydrochloric acid, and boiled until the evolution of gas ceases. When the precaution is taken to leave a little zinc undissolved, as pointed out before, the metallic precipitate remaining contains all the indium present with the lead. The residue is then dissolved in nitric acid, and the indium precipitated from the cold solution as oxide by means of barium carbonate. The oxide is reduced to the metal by ignition in a current of hydrogen.

The preparation of indium from indiferous zincblende is carried out by first roasting the mineral thoroughly, boiling the residue with dilute sulphuric acid, filtering, nearly neutralizing the filtrate with sodium carbonate, and then placing clean plates of zinc into the solution. The precipitate thus formed is removed from time to time from the zinc by scraping, thus facilitating the treatment for indium values according to the method indicated above.

To obtain indium in pure condition, the precipitate obtained by dissolving the spelter in acid and washing, is dissolved in nitric acid, part of the lead present removed by the addition of sulphuric acid, and the rest by means of hydrogen sulphide, together with metals of the second group like arsenic and cadmium or others. Potassium chlorate is then added to the filtrate from the sulphides, and the latter heated to boiling, the liquid cooled, and then treated with an excess of ammonia. In this manner much of the zinc present enters into solution, while a small amount is carried down by the precipitated iron and indium oxides. These are separated from the liquid by filtering, dissolving in dilute acetic acid, and the solution thus obtained again treated with hydrogen sulphide. This dissolving and precipitating operation is repeated seven times, when the still impure indium sulphide is dissolved in hydrochloric acid, and the ferric chloride present is reduced to the ferrous state by means of hydrogen sulphide. Barium carbonate is then added, to precipitate the oxide, which separates out within twenty-four hours, contaminated with the barium compound. This mixture is first heated at a low temperature and then at a higher degree of heat in a current of hydrogen, the gas being passed slowly, when the pure metal will be obtained in small silver-white globules, which are mechanically separated from the barium salt, and fused into a button under potassium cyanide.

DETECTION.—Roast the zincblende for two hours, dissolve it in hydrochloric acid, introduce metallic zinc, and boil the solution until the precipitation is complete. Filter, wash, dissolve the precipitate in aqua regia, and remove the metals of the second group by conducting hydrogen sulphide through the liquid to saturation. Filter and precipitate the indium, as oxide, In_2O_3, by barium carbonate. In order to remove any iron, eventually present, redissolve the precipitate, heat the solution with sodium sulphite, and digest with barium carbonate in a covered vessel. The oxide thus resulting may then be reduced to the metallic state by heating in a current of hydrogen.

QUALITATIVE DETERMINATION.—Indium and its compounds impart to the flame a peculiar bluish tint. When examined with the aid of the spectroscope two characteristic blue lines will be seen, a bright one in the blue, and a feebler one in the violet field of the spectrum. They are, however, very transient. The sulphide gives more persistent lines than the chloride.

H_2S produces no precipitate in the presence of a strong acid. Indium is, however, precipitated like the metal zinc, from slightly acid solutions, or in the presence of acetic acid. The slimy precipitate of indium sulphide, In_2S_3, is of a fine yellow color.

$(NH_4)_2S$ produces at first a white precipitate from a solution containing ammonium tartrate, said to consist of In_2S_3 and hydrogen, which turns yellow on the addition of acetic acid. The sulphide is insoluble in cold, but soluble in hot ammonium sulphide, and on cooling it separates out again of a white color.

NH_4OH, KOH or $NaOH$ produce a white bulky precipitate of indium hydrate. $In(OH)_3$, resembling aluminum hydrate, quite insoluble in NH_4OH or KOH. The presence of tartaric acid prevents the precipitation.

Alkaline carbonates precipitate white gelatinous carbonate. When recently precipitated it is soluble in ammonium carbonate, but not in the fixed alkaline carbonates. On boiling, indium carbonate separates out again.

CHAPTER XVII.

GALLIUM.

HISTORY.—Gallium was discovered in 1875 by the French chemist Lecoq de Boisbaudran in zincblende found near the town Pierrefitte, situated in the valley of Argeles, Hautes-Pyrenees, which contained about 0.002 per cent. of the metal. He named the new element "gallium" from Gallia, the Latin name of his country. His attention was called to the existence of the metal by two characteristic lines appearing in the spectrum, when testing the blende by the spectroscope. Mendelejeff had, as in the case of germanium, predicted the existence of gallium, judging from the gap occurring in the aluminum group of metals, as represented in the periodic system of the elements, and had foretold its atomic weight to be 68 and its specific gravity 5.8. In the beginning of his investigations Boisbaudran, who had only sixty milligrams of the metal at his disposal, found its specific gravity to be only 4.7 at 15° C.; later, however, when he was in possession of larger quantities of gallium, he determined the specific gravity of the metal as 5.9, a result which came very close to the figure predicted by the Russian chemist.

CHEMISTRY AND COMMERCIAL POINTS.—Gallium, of atomic weight 69 and specific gravity 5.9, is a bluish-white, hard and tough metal, which fuses at the extremely low temperature of 31° C. to a silver-white liquid. Hence it melts, if held in the hand, and has been found to adhere, when in this condition, to glass, forming a mirror of greater whiteness than that produced by tin amalgam. A globule of the molten metal may be kept in a fluid state for a long period, but will solidify into a crystalline mass, consisting of octahedra, as soon as touched by a crystal of gallium. The metal is slightly malleable, oxidizes superficially on exposure to the atmosphere, and does not volatilize appreciably at a red heat. Nitric acid has no effect upon gallium in the cold, but hydrochloric acid or a solution of potassium hydrate dissolve it readily, its behavior in this regard being similar to that of aluminum. It forms an ammonium alum of the generic formula $Ga_2(SO_4)_3\ (NH_4)_2\ SO_4+24H_2O$, but no such compound with potassium or sodium, and belongs to the aluminum or third group of the periodic system of the elements.

Gallium occurs in certain zincblendes, the richest being those of Luedrich and Apfel near Bensburg, Germany, which contain about one part in sixty thousand, and are of the black variety, commonly known as blackjack. Subsequently it was found to exist also in very limited quantities in zincblende of other localities, those from Asturia f. i. being known to contain appreciable amounts of the metal.

The extraction of gallium from its ores is accomplished by digesting the blende in a mixture of five parts hydrochloric and one part nitric acid, and boiling the solution thus obtained, until the greater part of the nitric acid is expelled, when slips of pure zinc are immersed in the solution, and withdrawn when the evolution of hydrogen has almost, but not entirely ceased. Most of the copper, lead, cadmium, iridium, thallium, silver, mercury, selenium and arsenic having been removed in this manner, a large excess of zinc is added to the clear fluid, which is then boiled for some hours, with the result that a bulky gelatinous precipitate comes down, containing alumina, basic salts of zinc and gallium. This precipitate is redissolved in hydrochloric acid, ammonium acetate is added, and the alumina precipitated with hydrogen sulphide. The hydrochloric acid solution of the white sulphides is fractionally precipitated with sodium carbonate, the gallium being found in the first portions. The point when the precipitation should be stopped is easily recognized by observing the spectrum of gallium, which is characterized by two violet lines.

The gallium is separated from the zinc, yet mixed with it, by solution in sulphuric acid and addition of excess of ammonia. Much of the gallium remaining dissolved in the ammonia, it is recovered by boiling till the excess of the latter is expelled. The excess of ammonium salts is then neutralized with aqua regia, and the gallium and zinc are separated by fractional precipitation with sodium carbonate. The pure gallium oxide precipitated by ammonia is dissolved in potash or in sulphuric acid under the addition of ammonia, and the solution decomposed electrolytically, when the metal gallium appears on the negative platinum electrode. Five or six Bunsen cells are able to decompose 20 or 30 c.c. of a strong solution, and the deposited metallic gallium is readily removed from the platinum electrode by bending it under cold water.

Metallic gallium is rather costly, since a gram of the genuine article brought $105 a few years ago, which figure has been reduced, however, to one-fifth, that is $21.

DETECTION.—Dissolve ten grams of the blende to be tested for gallium in aqua regia, expel the excess of acid by boiling, and introduce pure zinc into the solution in the cold. Filter the liquid while there is yet a notable evolution of hydrogen, and boil the filtrate with zinc. Wash the precipitate formed with water, dissolve it in hydrochloric acid, and test the solution, which has been concentrated as far as possible, by the spectroscope. If necessary the operation of boiling with zinc is repeated on the first white deposit formed.

QUALITATIVE DETERMINATION.—Metallic zinc withdraws readily one-sixth of a milligram of gallium from a litre of liquid, even in the presence of many foreign substances, the drawback being the difficulty of procuring really C. P. zinc. Metallic copper exacts the same sensitiveness in this respect as zinc, also cuprous oxide and cupric hydrate.

Potassium ferrocyanide precipitates very diminutive amounts of gallium from its solutions.

Hydrogen sulphide precipitates gallium only from acetate solutions.

QUANTITATIVE ESTIMATION.—This estimation consists in the isolation of the metal as indicated above, drying and weighing the metallic gallium.

CHAPTER XVIII.

VANADIUM.

HISTORY.—Vanadium, thus called from a surname of the Scandinavian goddess Freya, was discovered in 1830 by the chemist Sefstroem in a specimen of iron obtained from the ores at Taberg, Sweden, and was subsequently produced in larger quantities from the slags of the Taberg blast furnaces.

Del Rio, who previously analyzed the lead ore of Zimapan in Mexico, announced to have found a new metal in that mineral, which he called erythronium, meaning a kind of plant, since vanadic acid has a red color. In consequence of the demonstrations and objections of Collet Descotils, he changed, however, his opinion and declared that the metal was to be considered as an impure chromium. They were induced to this assumption by the color of chromic acid, which is also red.

After the discovery of vanadium by Sefstroem, Woehler proved first the presence of the metal in the Mexican ore, and Johnson identified later an ore occuring at Wanlockhead in Scotland as vanadinite.

In 1831 Berzelius investigated the compounds of vanadium more intimately, prepared also the metal, and characterized the element as being related to chromium and molybdenum.

This view was first attacked by Rammelsberg and Schabus, who showed that vanadinite is isomorphous with pyromorphite and apatite, and in 1867 Roscoe proved that the highest form of oxidation of vanadium was not VO_3 but V_2O_5, and also that vanadium did not belong to the series of chromium and molybdenum, but to that of phosphorus, arsenic and antimony. Vanadium is therefore found in the fifth group of the periodic system of the elements, which is headed by nitrogen and phosphorus.

Roscoe showed furthermore that the substance taken for free vanadium by Berzelius consisted partly of vanadium nitride and partly of the dioxide V_2O_2, and that the vanadium chloride of Berzelius had been actually a vanadium oxychloride, $VOCl_3$, analogous in composition to phosphorus oxychloride of the formula $POCl_3$. He also succeeded in preparing metallic vanadium in pure condition.

CHEMISTRY AND COMMERCIAL POINTS.—Vanadium of the atomic weight 51.2 and the specific gravity 5.5 is a light, grayish-white metal of silver-white luster, which is stable in air, and is not affected by water at ordinary temperatures. Its reduction from the pentoxide to the metallic state is best accomplished by heating the oxide in an electric furnace under the addition of reducing agents. It is not volatilized at a strong red heat, and is difficultly fusible, but burns brilliantly when heated in air or oxygen or thrown in powder form into a flame. The metal unites readily at a red heat with nitrogen, forming the mononitride, is insoluble in hydrochloric acid or aqueous alkalies, but is attacked by sulphuric acid, and readily dissolved by dilute or concentrated nitric acid. When fused with caustic soda, hydrogen is evolved, and sodium vanadate produced.

Vanadiferous iron ores are treated for their contents of the pentoxide V_2O_5 by mixing the finely powdered mineral with nitre, and heating the mixture in a fireclay crucible to complete fusion. The cooled mass, which contains the vanadium compounds present in the form of potassium vanadate, is then treated with boiling water, the solution thus obtained filtered, nearly neutralized with nitric acid, and mixed with a solution of barium chloride or nitrate, so as to precipitate the insoluble barium vanadate. This compound is separated from the liquid by filtration, washed with water and decomposed by heating with dilute sulphuric acid. The acid liquid thus resulting is then filtered from the precipitated barium sulphate, neutralized with ammonia, concentrated by evaporation on the water bath and cooled. Solid pieces of ammonium chloride are then introduced into the solution, when ammonium metavanadate, which is soluble in water, but insoluble in a concentrated solution of ammonium chloride, gradually separates out on prolonged standing. The vanadate thus obtained is then filtered off, washed with a concentrated solution of ammonium chloride, dried, and gently heated in an open crucible, when vanadium pentoxide of a rusty-red color remains, which may be brought to fusion by further heating and resolidified by cooling.

The vanadates and hypovanadates have found application in the printing of calico, and in fixing aniline-black on silken fabric. They are used for this purpose frequently in conjunction with sodium chlorate, when the vanadium compound present acts as an oxygen carrier in the formation of the aniline-black, only an extremely small quantity of the reagent being required for a large amount of aniline. To prepare a solution answering this purpose, the slags obtained in the course of the Thomas-Gilchrist process are sometimes employed. The latter serves for the elimination of phosphorus from the charge of iron ore in the converter, and the slags thus produced contain, in case the raw material employed is vanadiferous, frequently a percentage of vanadium approaching 1.5 per cent. In order to obtain these values from the slag, one kilo of the roughly broken material is treated with a litre of hydrochloric acid of 21° to 22° Beaume, which quantity is purposely chosen, as it is insufficient to decompose the entire amount of the slag. Without stirring the mass, three litres of water are then added, and the whole is allowed to react for two days. The solution thus resulting, which has a specific gravity of about 27° Beaume at 36° C., is decanted and diluted to 15° Beaume, when it may be used directly for the production of aniline-black.

The vanadates are also employed to some extent for the preparation of an indelible ink, which is obtained by the addition of gallic acid to a mixture of neutral ammonium metavanadate and gum water. The liquid thus produced is not attacked by acids, alkalies or chlorine, but does not appear to be quite permanent. Futhermore the oxides of vanadium are utilized in the decoration of porcelain and pottery, when they give a fine golden color of a greenish tinge, if fired in the enameling furnace at a high red heat.

In order to obtain the vanadium values contained in carnotite, which mineral was described under the caption "Uranium," the material, powdered to thirty mesh, is mixed with twenty per cent. of common salt, and the mass heated for half an hour at a gentle red heat in the bed of a reverberatory furnace, or, if working on a small scale, in an open roasting dish in an assayer's muffle. On lixiviating the sintered mass with the smallest amount of cold distilled water sufficient for solution, the vanadium values enter into solution as sodium vanadate, while the uranium compounds remain undissolved. The clear solution is then mixed with a calculated amount of caustic soda, which is dissolved in a small quantity of distilled water—all the distilled water used being obtained as a by-product—when sodium vanadate of a whitish color, and corresponding in composition to the formula Na_3VO_4 nH_2O is instantly precipitated. This salt settles readily in the precipitation vat, and is slightly washed with distilled water, after the removal of the supernatant liquid by means of a siphon pump. The product obtained in this manner is then dissolved in dilute nitric acid, and the hydrated vanadium pentoxide, which has a deep yellow color, precipitated from the solution by the addition of an excess of ammonia. The pentoxide, which is recovered in a partly dried condition by means of a filter or a filter press, represents the "vanadic acid" of the trade, and is brought on the market as such after further drying. This compound brought a few years ago $9 per pound, but has fallen in price to $1 for that quantity in consequence of the discovery of vanadium ores in Colorado.

The most important use of vanadium in manufactures consists, however, in its utilization as an alloying material for iron and steel, since the addition of a very small amount of the metal increases essentially the malleability and hardness of steel after tempering. In this manner a ready method is given for preparing sheet steel and armor plates possessing a very hard surface, but a soft interior. Even if only one-half per cent. of metallic vanadium to the ton is introduced into iron, its effect is such as to increase the tensile strength of the metal from 7.5 to 13 tons per square inch—a result which represents the mean of twenty-five experiments. These favorable results have led to the manufacture of metallic vanadium and ferrovanadium, which latter product is more readily incorporated into the bath of iron or steel to be improved, so that a limited demand for vanadium ores has been created, especially in the Liverpool and London markets. A complete analysis is, however, required by the English buyers beforehand, and since the concentration of vanadinite f. i. from its gangue appears to be accompanied with great difficulties, but little shipping has been done unto the present.

MINERALOGY.—Of the vanadium minerals roscoelite is the most important. It occurs in minute scales, and often in stellate or fan-shaped groups, which have a color verging between dark clove-brown to greenish-brown and dark brownish-green. Its structure is micaceous, its cleavage perfect, and its specific gravity varies between 2.92 and 2.94. The mineral is soft, has a pearly luster, and is translucent. It may be practically considered as a vanadium aluminum silicate. Before the blowpipe it fuses easily to a black glass, and gives with salt of phosphorus a dark yellow bead in the oxidizing flame, while the latter assumes an emerald green coloration in the reducing flame.

The composition of roscoelite is given by the following analytical data:

SiO_2	41.25	per cent.
V_2O_5	28.85	per cent.
Al_2O_3	14.34	per cent.
Fe_2O_3	1.04	per cent.
Mn_2O_3	1.45	per cent.
MgO	1.96	per cent.
CaO	0.61	per cent.
K_2O	8.25	per cent.
Na_2O	0.72	per cent.
H_2O	3.06	per cent.
	101.53	

Specific gravity, 2.902.

A variety of roscoelite is said to occur in the Magnolia district, Colorado, as a thin earthy incrustation of a grayish to olive-green color on calaverite, and inclosed in quartz, to which it imparts a green color. An analysis of this variety gave:

SiO_2	56.74	per cent.
Al_2O_3	19.62	per cent.
V_2O_5	7.78	per cent.
FeO	3.84	per cent.
MgO	2.63	per cent.
Na_2O	0.94	per cent.
K_2O	8.11	per cent.
MnO	Trace	
Li_2O	Trace	
	99.66	

Roscoelite is furthermore known to occur at Granite creek, near Coloma, Eldorado county, California, where it is found intimately mixed with gold in seams one-tenth to one-twentieth inch thick in porphyry, and filling cavities in quartz. Its occurrence has also been observed at the Big Red ravine, near Sutter's mill, and at the Granite creek locality, California.

Roscoelite occurs also associated with carnotite in the Placerville district, San Miguel county, and in the western part of Montrose county, Colorado, as stated under "Uranium." The percentages of vanadium pentoxide, contained in the roscoelite of these two localities, vary between twenty-one in Montrose county and thirteen near Placerville for very rich ore, the percentage of V_2O_5 being as a rule one-fifth of the contents in uranium oxide.

Another vanadium mineral, known as vanadinite, occurs in commercial quantities in Arizona and New Mexico. It is virtually a vanadate of lead combined with an inferior portion of lead chloride, the pure mineral containing 90.3 per cent. of the former, and 9.7 per cent. of the latter. The Arizona and New Mexico varieties show the following composition, the presence of arsenic and phosphorus pentoxide in the mineral being usual:

Vanadinite from Arizona.		Vanadinite from New Mexico.	
V_2O_5	16.98 per cent.	V_2O_5	17.37 per cent.
As_2O_5	3.06 per cent.	As_2O_5	0.24 per cent.
P_2O_5	0.29 per cent.	P_2O_5	0.57 per cent.
PbO	77.49 per cent.	PbO	79.43 per cent.
Cl	2.41 per cent.	Cl	2.39 per cent.
Fe_2O_3	0.48 per cent.	Fe_2O_3	None
	100.71		100.00
Specific gravity, 6.572.		Specific gravity, 6.862.	

The mineral is found principally at the Hamburg and Melissa mines in Yuma county, at the Vulture and Phœnix in Maricopa county, at the Black Prince and Mammoth, Pinal county, and in the Humbug district, Yavapai county, Arizona. In New Mexico it occurs at Lake Valley, Sierra county, and in the Mimbres mines near Georgetown. It is met with furthermore, but only sparingly, in Montana at the Bald Mountain mine, in Beaver county.

A variety of vanadinite, known as endlichite, and thus named from Dr. F. M. Endlich, occurs at Lake Valley. It varies from vanadinite mainly by its lesser percentage in vanadium pentoxide and its higher contents in arsenic pentoxide, as will become evident from the analytical data given below:

V_2O_5	7.94	per cent.
As_2O_5	10.73	per cent.
P_2O_5	None	
PbO	79.15	per cent.
Cl	2.18	per cent.
	100.00	

Vanadinite itself crystallizes mostly in hexagonal prisms, which have smooth faces and sharp edges, but is found also in rounded forms in incrustations, and in parallel groupings. The fracture of the mineral is uneven, its hardness 2.75 to 3, its specific gravity 6.66 to 7.23, its fractured surfaces resinous, and its color verges from deep ruby-red to light brown, yellow and reddish-brown. Its streak is white or yellowish. It is brittle, subtranslucent or opaque.

Finally a third vanadium mineral, known as descloizite, and thus named from the French mineralogist Descloizeaux, deserves mention. It is to be considered as a vanadate of lead, though it contains as a rule admixtures of iron, zinc, copper, manganese and sand, which are to be regarded as impurities. The following analysis will make these points more clear:

V_2O_5	22.46 per cent.
PbO	54.70 per cent.
ZnO	2.04 per cent.
CuO	0.90 per cent.
FeO	1.50 per cent.
MnO	5.32 per cent.
Mn_2O_3	6.00 per cent.
Cl	0.32 per cent.
H_2O	2.20 per cent.
Sand	3.44 per cent.
	98.88

Descloizite occurs in the Sierra de Cordoba, Argentine Republic, in small crystals of olive-brown or green to black color, which appear on the edges light-brown to red by transmitted light. They have a bright luster, a hardness of 3.5, a specific gravity of 5.839, and occur usually clustered unto a ferro-silicious gangue in association with pyromorphite. Particles of these crystals behave, when introduced into the salt of phosphorus bead before the blowpipe flame, in the same manner as the vanadium minerals described above.

The mineral is found in abundance, and frequently associated with vanadinite and wulfenite, in some of the mines of New Mexico and Arizona, among them being the Sierra Grande mine, Lake Valley, Sierra county, and the Mimbres mine, near Georgetown, New Mexico. In Arizona it occurs near Tombstone; in Yavapai county, and in the Mammoth gold mine, near Oracle, Pinal county. It is met with sparingly at the Wheatley mine, Phenixville, Pennsylvania, and varieties are found at the Mayflower mine, Bald Mountain district, Beaverhead county, Montana, also in San Luis Potosi and Zacatecas, Mexico, and in the Lucky Cuss mine, Tombstone, Arizona.

DETECTION.—Vanadium compounds are recognized by the yellow color which they impart to the salt of phosphorus bead in the oxidizing flame of the blowpipe, and by the emerald-green tint produced in the reducing flame.

Another manner of detecting vanadium consists of the following operations: Powder the ore supposed to contain vanadium, finely, weigh off eight grams, mix them with thirty-two grams of sodium carbonate and fuse the mixture thoroughly in a fireclay crucible in the muffle. Let cool, add a small quantity of potassium nitrate, and heat to a dull red heat, taking care not to heat any higher. Lixiviate the cooled mass with water, filter, boil the clear solution with ammonium carbonate, and filter off the silica. Acidify the filtrate with hydrochloric acid, evaporate strongly, and pass hydrogen sulphide through the liquid to remove metals of the second group. Filter, heat the filtrate with an equal volume of concentrated ammonia, and pass hydrogen sulphide through the solution till the free ammonia is completely saturated. In case vanadium is present, the liquid assumes an intense cherry red color. The liquid may then be filtered, the filtrate neutralized with hydrochloric acid, and the precipitate thus produced, consisting of sulphur and vanadium sulphide, separated from the liquid by filtration, washed, dried and ignited, and the residue fused with potassium nitrate. The fused mass contains potassium vanadate and from it the characteristic blowpipe reactions, mentioned above, are obtained.

QUALITATIVE DETERMINATION.—The borax bead dissolves vanadium pentoxide to a clear bead, colorless or, with large quantities of the anhydride, yellow in the outer flame, beautiful green in the inner flame. With large quantities of vanadic acid it looks brownish, white hot, and only turns green on cooling.

Orthovanadates are generally yellow or reddish-yellow both in the liquid and solid state. By boiling in water, the orthovanadates of the alkalies are converted into colorless metavanadates. On the addition of an acid to a solution of neutral or orthovanadate, the solution becomes yellowish-red, owing to the formation of anhydrous salts.

Ammonium, barium and lead vanadates are but sparingly soluble in water. The alkaline vanadates are more soluble in pure water than in water containing free alkali or a salt; hence they are precipitated in the presence of the latter. All are soluble in nitric acid, but insoluble in alcohol.

$(NH_4)_2S$ produces a brown coloration in a solution of metavanadates, and, on acidulating with hydrochloric acid, or better sulphuric acid, the soluble ammonium sulphovanadate is decomposed, and brown pentasulphide, V_2S_5, mixed with sulphur, is precipitated; the liquid at the same time generally acquires a blue color. It dissolves with red-brown color in aqueous solutions of alkaline carbonates, hydrates and sulph-hydrates.

Vanadic anhydride has a reddish-yellow color, and is difficultly soluble in water (1,000 parts), forming a light yellow solution, which reddens litmus paper. It dissolves also in the stronger acids to red or yellow solutions, which become frequently decolorized by mere boiling. It unites, however, with bases more readily than with acids. Alkaline vanadates are soluble in water, inversely to the quantity of free alkali or alkaline salt present. Hence they are precipitated from their solutions by excess of alkali, or by salts, especially by excess of ammonium chloride. (Most characteristic reaction.)

A sulphuric acid solution of vanadium pentoxide, when considerably diluted with water and treated with zinc, or sodium amalgam and warmed gently, turns first blue, then green, and finally from lavender to violet. The V_2O_5 becomes reduced to V_2O_2, and on the addition of ammonia a brown precipitate of the hydrated dioxide (hypovanadious acid) forms, which absorbs oxygen more rapidly than any other known reducing agent, and bleaches organic coloring matter (indigo solution f. i.) as quickly as chlorine.

Many organic substances, such as oxalic or tartaric acid, sugar and alcohol, reduce vanadic acid, especially in the presence of strong mineral acids, to the blue V_2O_4. The same reaction takes place when

SO_2 or H_2S are added to its solutions in acid.

If an acidified solution of an alkaline vanadate be shaken up with ether containing hydrogen peroxide, the aqueous fluid acquires a red-brown color, like that of ferric acetate, while the ether remains colorless. This reaction is extremely delicate.

Vanadic and chromic acids are the only acids whose salts give rise to red-colored solutions. They are, however, differently affected by reducing agents.

QUANTITATIVE ESTIMATION.—Mix two to five grams of the finely pulverized vanadiferous ore with one-third of its weight of potassium nitrate in a fire-clay crucible, and expose it to a gentle, low red heat in the muffle for an hour, taking care not to surpass that temperature. Crush the fused mass, and extract it with as small amount of water as possible, filter, and add carefully dilute nitric acid, stirring constantly, until the solution is slightly alkaline. (If the liquid is made acid, the vanadic acid present will be reduced by the liberated nitrogen dioxide—a condition which is to be avoided.) Filter off the silica and alumina separated out, add a solution of barium chloride and some ammonia, allow to settle, filter off the precipitate of barium vanadate (accompanied in cases by barium sulphate), wash, and boil it with a small excess of dilute sulphuric acid. Filter, wash first with water, and finally with dilute ammonia and water, saturate the filtrate completely with ammonia, if not already neutral, condense to half the bulk of the liquid, cool and place lumps of ammonium chloride into the solution. In proportion as the liquid becomes saturated with the ammonium chloride, the metavanadate of ammonium separates out in form of a white or yellowish crystalline powder. It is advisable, therefore, to let stand over night. Filter, wash with a saturated solution of ammonium chloride, dry, incinerate in an open platinum or porcelain crucible, and weigh the vanadium pentoxide remaining, which may be fused at a high heat, and allowed to cool to a crystalline mass.

(See Appendix.)

CHAPTER XIX.

BERYLLIUM.

HISTORY.—As early as 1797 the French chemist Vauquelin recognized an unknown earth in the mineral beryl, and called that body "glucine" (meaning sweet earth), on account of the sweet taste peculiar to its salts. This appellation for the base and the term "glucinum" for the element derived therefrom have been preserved in France and England, but not in the United States, where the name beryllium instead of glucinum is generally accepted. In 1828 Woehler and Bussy succeeded first in isolating metallic beryllium by fusing the chloride with potassium in a platinum crucible, though the product thus obtained was pulverulent and impure. A few years later Becquerel produced the metal in purer condition by electrolyzing a solution of the chloride, and in 1854 Debray obtained pure beryllium by conducting the vapors of the chloride over fused sodium in an atmosphere of hydrogen. The metal produced by Debray was white in appearance, and could be forged and rolled into sheets like gold.

CHEMISTRY AND COMMERCIAL POINTS.—Beryllium of the atomic weight 9.1 and specific gravity 2.1 is a white, ductile metal, whose fusing point lies near 950° C. It melts in the outer blowpipe flame, without igniting like zinc or iron, and does not burn, when heated in an atmosphere of oxygen, but covers itself with a layer of oxide, which appears to prevent further change. If heated, however, in very finely divided form in the air, it burns with an extremely bright light. The metal shows but very little affinity for sulphur, but combines, when heated, directly with chlorine and iodine. It unites readily with silicon, forming a hard, brittle substance, which takes a high polish. Beryllium does not decompose water at a boiling heat, or even when heated to whiteness. Sulphuric and hydrochloric acids dissolve it with evolution of hydrogen, and also potassium or sodium hydroxides. Nitric acid does not affect it at ordinary temperatures, but dissolves it slowly at the boiling heat. Beryllium forms a double salt, of the formula $BeSO_4$ $K_2SO_4+3H_2O$, which is difficultly soluble in water, and resembles the alums.

Many of the natural beryllium compounds, like emerald, chrysoberyl, aquamarine and others described below are valued as gems, when perfectly colored or finely crystallized, and are, therefore, highly prized in trade. Artificial beryllium or its compounds have, however, not found any commercial application unto the present. The metal may be bought from retailers at $2.50 for one-tenth gram of the crystallized variety, and at $1.50 for the powdered metal while the nitrate is sold at $20 per pound.

Mineralogy.—Beryllium is not very abundant in nature, and occurs chiefly as a double silicate of aluminum and beryllium of the formula $Al_2Be_3 (SiO_3)_6$, which in its rough form is called beryl. Its composition, when pure, is represented by the figures:

SiO_2	67.0	per cent.
Al_2O_3	19.0	per cent.
BeO	14.0	per cent.
	100.0	

Beryl is a common accessory mineral in granite veins and especially in those of a pegmatitic character. In the United States rough beryls of gigantic dimensions have been found at Acworth and Grafton, New Hampshire, and at Royalston, Massachusetts, one of them from Grafton weighing 2,900 pounds, and another from the same locality 1,076 pounds. Albany, Maine; Haddam, Connecticut; Leiperville and Chester, Pennsylvania; Stony Point, North Carolina; Amelia Court House, Virginia; Coosa county, Alabama, and the Black Hills, South Dakota, are furthermore known as places of occurrence. Beautiful hexagonal crystallizations of beryl, embedded in pegmatite (graphic granite), are found in Jefferson county, Colorado, and bluish-green aquamarines occur near the summit of Mount Antero, Chaffee county, of that state.

The composition of common beryl is indicated by the following analytical data:

SiO_2	65.54 per cent.
Al_2O_3	17.75 per cent.
Fe_2O_3	0.21 per cent.
FeO	0.38 per cent.
BeO	13.73 per cent.
CaO	0.06 per cent.
Na_2O	0.71 per cent.
Li_2O	Trace
H_2O	2.01 per cent.
	100.39

Specific gravity, 2.706.

The mineral occurs usually in long prismatic crystals, rarely in tabular aggregations, and occasionally in large columnar or granular masses. Its cleavage is imperfect, and its fracture conchoidal to uneven. It is brittle, transparent to translucent, and has a hardness of 7.5 to 8, a specific gravity varying between 2.6 and 2.8, and a vitreous, but sometimes resinous lustre. Its color verges from emerald-green into pale green, light blue, yellow and white, and occasionally into pale rose-red. Its streak is white. Numerous varieties occur, however, which are distinguished by their color as aquamarines, a bluish-green beryl, golden beryl of a clear bright yellow, and emerald, a precious stone, colored green by a slight amount of chromic oxide. An analysis of the latter gave the following data:

SiO_2	67.85 per cent.
Al_2O_3	17.95 per cent.
Cr_2O_3	Trace
BeO	12.40 per cent.
MgO	0.90 per cent.
Na_2O	0.70 per cent.
H_2O	None
	99.80

Beryllium occurs furthermore as a simple silicate in the mineral phenacite, corresponding in composition, when pure, to the formula Be_2SiO_4, and consisting then of:

SiO_2	54.45 per cent.
BeO	45.55 per cent.
	100.00

This mineral is met with at Topaz butte, near Florissant, sixteen miles from Pike's Peak, Colorado, where it is found in flat rhombohedral crystals with topaz on amazonstone or embedded in the latter. Amazonstone or amazonite is a verdigris green colored aluminum, potassium, sodium silicate, containing sometimes small percentages of ferric iron, lime and magnesia. Phenacite occurs also at Mount Antero, often in prismatic crystals, and associated with quartz and beryl. In the East it is found on Bald Face mountain, North Chatham, New Hampshire, and also at the mica mines of Amelia Court House.

The crystals of phenacite are usually rhombohedral, sometimes lenticular, and in cases prismatic. Their cleavage is indistinct, and the fracture conchoidal. The mineral is brittle, transparent to translucent, its hardness lies between 7.5 and 8, and its specific gravity between 2.97 and 3. Its lustre is vitreous, and its color verges between brown, pale rose-red, wine-yellow, and colorless. A specimen from Florissant of specific gravity 2.96, analyzed as follows:

SiO_2	54.44	per cent.
BeO	45.58	per cent.
Na_2O	0.21	per cent.
Li_2O	Trace	
Ignition	0.26	per cent.
	100.49	

Beryllium forms also a constituent of the mineral chrysoberyl, a beryllium aluminate of the composition BeO Al_2O_3, and is present in euclase, a hydrated aluminum beryllium silicate, corresponding to the formula Be(AlOH) SiO_4. When in pure condition, these two minerals consist of 80.2 per cent. Al_2O_3 and 19.8 per cent. BeO, and 41.3 per cent. SiO_2, 35.2 Al_2O_3, 17.3 BeO, and 6.2 per cent. water respectively.

DETECTION.—The reactions of beryllium are in most respects similar to those of aluminum. A sufficient distinction between the two is, however, afforded by the action of ammonium carbonate, which dissolves the precipitates formed by alkalies and alkaline carbonates, but not the corresponding precipitates of aluminum. Furthermore beryllium compounds, when moistened with cobalt nitrate, and heated before the blowpipe, give a gray mass, but not the blue color characteristic of aluminum compounds.

QUALITATIVE DETERMINATION. — NH_4OH and $(NH_4)_2S$, as well as the fixed caustic alkalies and alkaline earthy bases precipitate beryllium hydrate $Be_2(OH)_6$ flocculent, soluble like $Al_2(OH)_6$ in excess of the fixed alkalies, but not in ammonia. On boiling $Be_2(OH)_6$ is almost completely reprecipitated from a dilute NaOH or KOH alkaline solution. (Distinction from Al_2O_3.) Like Al_2O_3 it is reprecipitated also on the addition of NH_4Cl.

$(NH_4)_2CO_3$ gives a white precipitate of basic beryllium carbonate, freely soluble in excess, reprecipitated as basic carbonate on boiling. (Distinction from Al_2O_3.)

Na_2CO_3 or K_2CO_3 precipitate also white carbonate, soluble only in large excess of the precipitant.

$BaCO_3$ precipitates beryllium completely, even in the cold. If the readily soluble beryllium sulphate is brought together with potassium sulphate, the difficultly soluble double sulphate of the formula $BeK_2(SO_4)_2+3H_2O$ is produced.

QUANTITATIVE ESTIMATION.—Mix one gram of the finely powdered beryllium mineral with four grams of potassium carbonate, place the mixture into a fireclay crucible, and expose it to a full white heat for two hours. Treat the fused mass with water and hydrochloric acid, and evaporate to dryness to separate the silica, as usual. Filter and precipitate the beryllia, alumina and ferric oxide in the filtrate with ammonia. Filter, wash and boil the precipitate with a concentrated solution of ammonium chloride as long as ammonia is liberated, frequently renewing the water. Filter and precipitate the beryllium hydroxide Be $(OH)_2$, which alone is dissolved, in the filtrate by ammonia, filter, dry, incinerate and weigh as BeO.

CHAPTER XX.

THORIUM.

History.—This rare element was discovered in 1828 by Berzelius in a black mineral, resembling obsidian, found near Esmark, a town situated on the Norwegian island Loevoe, and was called by him "thorium" from the ancient Swedish deity Thor. Subsequently Woehler proved the presence of thorium in pyrochlore, while Karsten discovered it in monazite. A mineral very similar to thorite and known as orangite, occurring in Brevig, Norway, was later shown by Bergemann and others to contain thorium, and finally Mosander and Chydenius found the element in euxenite from Arendal, while Bahr proved its presence in gadolinite, orthite and in another mineral resembling the latter. Bahr imagined first to have discovered a new element, and called it "wasium," but acknowledged subsequently its identity with thorium.

Chemistry and Commercial Points.—Thorium of the atomic weight 232.4 and specific gravity 7.7 has an iron-gray metallic lustre, and is usually obtained by heating anhydrous thorium chloride of the formula $ThCl_2$ with potassium or sodium, the reduction of the salt to the metallic state being accomplished by slight detonation. When produced, in this manner, thorium forms a gray metallic powder, which may be pressed together by a polished agate to a more solid metallic body. When heated in contact with the air it burns with great brilliancy, producing snow-white thoria ThO_2. The element is not affected by hot or cold water, dissolves readily in nitric acid, slowly in hydrochloric and gradually in sulphuric acid. It is not attacked by solutions of caustic alkali.

The oxide of thorium has become commercially important by its peculiar property of producing an incandescent light, when heated in burning illuminating or other gas, while the minerals containing thorium are highly valued and much sought for. They serve for the preparation of the mantles of Welsbach's incandescent lights, which are made by saturating a network of cotton with a solution of the combined nitrates, oxides or bromides of thorium and other rare earths, as explained below. The supporting cotton webs are then incinerated by heating, the salts being thus changed into oxides and the mantles shaped to the proper form. Of the oxides known to be applicable for this purpose, that of thorium is the most desirable in the body of the mantle, since it increases greatly the illuminating power of the latter, while the oxide of lanthanum, without the presence of sufficient thoria, renders the mantle flexible, and is therefore hurtful. The illuminating power of thoria is furthermore favored by the addition of a small amount of uranium or cerium oxides, when the light produced is more vivid and nearly white, in spite of the fact that thorium oxide radiates but little light, which is yellow in color, and uranium oxide alone gives off but little luminosity, which is yellowish red.

In recent years Welsbach discovered that the illuminating power of lanthanum, cerium, yttrium, zirconium and other refractory earths is greatly increased by the addition of thoria, that ceria gives not only a desirable yellow light, but greatly increases the life of the mantle by causing it to preserve its desired shape, and renders it stronger and more durable in every respect. Finally Welsbach established the fact that the minimum consumption and the greatest efficiency is produced by a mixture of ninety-nine per cent. thoria and one per cent. ceria. In connection with the foregoing it is remarkable to note that the price of a kilogram of thorium nitrate fell from $400 in 1894 to $300 in 1895, to $200 in 1896, to $16 during the course of the next few years, to $10 in 1900, and to $6.50 in 1901. Metallic thorium sells at $20 per gram.

MINERALOGY.—Thorite, a thorium mineral, which may be considered, when pure, as a thorium silicate, consisting of 18.5 per cent. SiO_2 and 81.5 per cent. thoria, occurs in square prisms, but also massive and compact, is brittle, of distinct cleavage, conchoidal fracture, of vitreous to resinous lustre, and has a hardness ranging between 4.5 to 5, and a specific gravity of 4.4 to 4.8. The specific gravity of orangite, a nearly related mineral, varies between 5.19 and 5.40. The color of these two minerals, which differ from each other mainly by the amount of water they contain, is sometimes orange or brownish-yellow (orangite), but in cases brown inclining to black (thorite). Their streak is light orange to dark brown, and their splinters, when thin, are nearly opaque. Orangite is found occasionally in bright, orange-yellow tetragonal crystals, and forms frequently the kernel of a crystal externally altered to thorite. Uranothorite, which occurs mostly in massive form, has a subconchoidal fracture, a hardness equalling 8, a specific gravity 4.126, resinous to subvitreous luster, dark red-brown color, a yellow-brown streak, and is infusible before the blowpipe. It occurs in the Champlain iron region of northern New York. Thorite and orangite are known to occur in several localities of Norway, but have not as yet been found in the United States. The following analytical results will give an idea of the composition of these minerals:

Thorite.

SiO_2	18.98 per cent.
ThO_2	57.91 per cent.
U_2O_3	1.58 per cent.
PbO	0.80 per cent.
Fe_2O_3	5.79 per cent.
Al_2O_3	0.06 per cent.
CaO	2.58 per cent.
MgO	0.36 per cent.
K_2O	0.24 per cent.
H_2O	9.50 per cent.
SnO_2	0.01 per cent.
Insoluble residue	1.70 per cent.
	99.51

Specific gravity, 4.8.

Orangite.

SiO_2	17.52 per cent.
ThO_2	71.65 per cent.
U_2O_3	1.13 per cent.
PbO	0.88 per cent.
Fe_2O_3	0.59 per cent.
Al_2O_3	0.17 per cent.
CaO	1.59 per cent.
MgO	Trace
K_2O	0.47 per cent.
H_2O	6.14 per cent.
	100.14

Specific gravity, 5.19.

Uranothorite (from Lake Champlain).

SiO_2	19.38 per cent.
ThO_2	52.07 per cent.
UO_3	9.96 per cent.
PbO	0.40 per cent.
Fe_2O_3	4.01 per cent.
Al_2O_3	0.33 per cent
CaO	2.34 per cent.
MgO	0.04 per cent.
K_2O	0.11 per cent
H_2O	11.31 per cent
	99.95

Specific gravity, 4.126.

A mineral, known as auerlite, and thus named from Dr. Carl Auer von Welsbach of Vienna, the inventor of the incandescent mantle light, occurs in disintegrated granite or gneiss, and associated with zircon, in Henderson county, North Carolina, at the

Freeman mine, Green river, and on Price land, three miles southwest. It is of dull yellowish white to dark orange-red color, crystallizes in square prisms with pyramids, has a hardness 2.5 to 3, specific gravity 4.42 to 4.77, resinous lustre, and is in appearance translucent to opaque. Auerite is infusible before the blowpipe, becomes brown on ignition and turns orange again on cooling. It analyzes as follows:

SiO_2	7.64 per cent.
P_2O_5	7.46 per cent.
ThO_2	70.13 per cent.
Fe_2O_3	1.38 per cent.
CaO	0.49 per cent.
MgO	0.29 per cent.
Al_2O_3	1.10 per cent.
H_2O CO_2	11.21 per cent.
	99.70

Another mineral of this class is monazite, and also monazite sand, which latter occurs in large deposits in Brazil. They contain considerable amounts of thorium, and the prices paid for the different kinds of monazite or monazite sand are fixed according to the percentages of thorium present in them. The highest grades of the mineral have been obtained from Burke, Poke, McDowell and Rutherford counties, North Carolina, which showed a percentage of 4 to 6.5 in thoria, while further deposits occur at Amelia Court House, Virginia. The average monazite contains from 2.5 to 3.5 per cent. of thoria, the remainder consisting of the oxides of cerium, didymium, erbium, lanthanum, yttrium and zirconium. The mineral is essentially a phosphate of the cerium metals, corresponding to the formula $(Ce\ La\ Di)PO_4$, most analysis showing usually the proper amounts of thoria and silica to form thorium silicate. Analytical data, given below, will illustrate these points more clearly.

Monazite from Burke county, North Carolina:

P_2O_5	29.28 per cent.
Ce_2O_3	31.38 per cent.
La_2O_3 Di_2O_3	30.88 per cent.
SiO_2	1.40 per cent.
ThO_2	6.49 per cent.
Ignition	0.20 per cent.
	99.63

Specific gravity, 5.10.

The mineral is rather abundantly distributed as an accessory constituent of gneissoid rocks in certain regions, thus in North Carolina and Brazil. It is infusible before the blowpipe, but turns gray, when thus treated, and, if moistened with sulphuric acid, it colors the flame bluish-green. With borax it gives a bead, yellow when hot, and colorless on cooling, while a saturated bead becomes enamel-white on flaming. It is difficultly soluble in hydrochloric acid. Monazite is thus named from the Greek term, meaning "to be solitary," in allusion to its rare occurrence.

A single grain of monazite can be rapidly and securely identified by moistening it with sulphuric acid on a slip of glass, and driving off the acid by heat. The cerium will then crystallize in double ball-shaped clusters of radiating needles or minute isolated crystals shaped like cucumber seeds. This crystallization is better shown by the addition of a drop of water, and allowing the crystallization to take place in a dessicator. Another drop of water with a little ammonium molybdate gives on evaporation a satisfactory test for phosphoric acid.

A further mineral, containing thoria, and related to samarskite, which latter was named after the Russian Samarski, has been found in the granite debris of Devil's Head mountain, Douglas county, Colorado, in small fragments of chestnut size, showing faint suggestions of a crystalline form. It is very brittle, of subconchoidal fracture, hardness 5.5 to 6, specific gravity 6.18, has a vitreous luster, a pitch-black color, which appears pale-brown in thin splinters, and has a dirty-brown streak. Before the blow-pipe it becomes dull, but does not fuse; it is slightly soluble in hydrochloric acid. Of the specimens examined, the first of which has been described above, the second had a salmon-colored streak, and the third seemed to be much altered. Analyses gave the following data:

	No. 1. Per Cent.	No. 2. Per Cent.	No. 3. Per Cent.
Nb_2O_5	27.77	26.16	27.56
Ta_2O_5	27.03	28.11	19.34
WO_3	2.25	2.08	5.51
SnO_2	0.95	1.09	0.82
ZrO_2	2.29	2.60	3.10
UO_2	4.02	4.22	6.20
ThO_2	3.64	3.60	3.19
Ce_2O_3	0.54	0.49	0.41
$(DiLa)_2O_3$	1.80	2.12	1.44
Er_2O_3	10.71	10.70	9.82
Y_2O_3	6.41	5.96	5.64
Fe_2O_3	8.77	8.72	8.90
Oxides FeO, MnO, ZnO, PbO, CaO, K_2O and $(NaLi)_2O$	2.55	2.60	4.31
H_2O	1.58	1.30	3.94
	100.31	99.75	100.18

Detection.—Thorium dioxide, when heated before the blowpipe, remains infusible; it imparts no tinge to the flame, and gives a colorless borax bead. It yields no characteristic reaction with cobalt nitrate.

Qualitative Determination.–NH_4OH or $(NH_4)_2S$ precipitate the white gelatinous hydrate $Th(OH)_4$, insoluble in excess.

KOH or NaOH produce the same precipitate, insoluble in excess. (Distinction from Al and Be.)

Ammonium, potassium and sodium carbonates precipitate white basic thorium carbonate, readily soluble in excess of the reagents, difficultly soluble in dilute solutions. (Distinction from Al.) From a solution in $(NH_4)_2$ CO_3 thorium carbonate is reprecipitated even at 50° C.

$BaCO_3$ precipitates thorium salts completely in the cold.

Oxalic acid produces a white precipitate (distinction from Al and Be), not soluble in excess nor in dilute mineral acids; soluble in ammonium acetate containing free acetic acid. (Distinction from Y and Ce.)

HFl precipitates gelatinous thorium tetrafluoride, $ThFl_4$, which becomes pulverulent after some time; the precipitate is insoluble in water and in HFl. (Distinction from Al, Be, Zr and TiO_2.)

$Na_2S_2O_3$ precipitates thorium hyposulphite $Th(S_2O_3)_2$, mixed with sulphur, from neutral or acid solutions. The precipitation is not complete. (Distinction from Y, Er and Di.)

A boiling concentrated solution of K_2SO_4 precipitates slowly, but completely, the whole of the thorium sulphate as white crystalline insoluble potassium thorium sulphate $K_4Th(SO_4)_4+2H_2O$ (distinction from Al and Be), soluble with difficulty in cold, and also in hot water, but readily soluble on the addition of some HCl.

Quantitative Estimation.—One gram of the finely pulverized thorium mineral (thorite) is heated with hydrochloric acid, the latter being renewed six times ,if necesary, so as to decompose the ore completely, and the whole evaporated to dryness on the water bath. The silica is then separated in the usual manner and hydrogen sulphide conducted through the filtrate to saturation, when the liquid is allowed to settle. It is then filtered from the small precipitate containing tin and lead, and the filtrate evaporated to a small volume. After cooling, ammonia is added to neutralization, and the precipitate, consisting mainly of thoria, iron and alumina, filtered off, washed well, dissolved in dilute sulphuric acid, and the solution thus obtained, evaporated on the water bath, when, on concentrating, a white voluminous mass separates out, which is neutral thorium sulphate, slightly soluble in hot water. The mother liquid is then filtered off, and the salt remaining on the filter washed with boiling water, dried and ignited, when pure thoria remains. The filtrate is concentrated by evaporation on the water bath, neutralized with potassium carbonate, and mixed with a boiling saturated solution of potassium sulphate, when, on cooling, a double salt of potassium thorium sulphate crystallizes out, which is insoluble in a concentrated solution of potassium sulphate. It is, therefore, brought on a filter, washed with such a solution, dissolved in warm water, and the liquid resulting treated with ammonia to precipitate the thoria, which is filtered off, washed, ignited and weighed as ThO_2. The weight obtained in this manner is added to the first weight of thoria found.

CHAPTER XXI.

ZIRCONIUM.

HISTORY.—The element zirconium was named from the rare mineral zircon, a silicate of the formula $ZrSiO_4$, when pure, in which the German chemist Klaproth discovered the presence of zirconia, ZrO_2, in 1789. In the year 1845 the chemist Svanberg announced to the Swedish Academy of Science to have ascertained by a closer study of zirconia, that it consisted of a mixture of two distinct earths. To the element present in one of these he gave the name "norium." Several chemists, among them Berlin, Marignac and Hermann, made diligent researches subsequently in order to settle the point in question, but having failed to verify it, pronounced the statement of Svanberg erroneous. In later years the chemist Sorby thought to have recognized in zirconia by means of spectrum analysis the presence of a new element, which he called "jargonium," a term derived from "jargon." The latter name is applied in mineralogy to the colorless and yellowish or smoky zircons from Ceylon. The chemist Forbes fell into the same error as Sorby, but both admitted later that the peculiar dark bands of the spectra of these zircons were due to the presence of a small quantity of uranium.

Zirconium has since been found in hyacinth, eudialyte, polymignite and other rare minerals.

CHEMISTRY AND COMMERCIAL POINTS.—Metallic zirconium of the atomic weight 90.7 and specific gravity 4.15, may be obtained in several allotropic modifications, as amorphous, crystalline and graphitoidal. The first variety is prepared by heating sodium zirconium chloride in a crucible with sodium or potassium, when it forms an amorphous powder, which may be compressed into thin lustrous laminæ, resembling graphite. Crystalline zirconium results on heating one part of potassium zirconium fluoride with one and a half parts of metallic aluminum in a graphite crucible to about 1200° C. When the crucible has cooled, the surface of the aluminum is found to be covered with foliated crystalline laminae, consisting of nearly pure zirconium, which may be separated by dissolving the aluminum with hydrochloric acid. The modification thus obtained is very hard. It fuses at a temperature produced by the oxyhydrogen flame or by that of the electric furnace. Graphitoidal zirconium is prepared by decomposing sodium zirconate with iron, when it is obtained in the form of small very light scales of a steel-gray color.

Zirconium is but slowly attacked by sulphuric or hydrochloric acid, even when heated, but hot aqua regia and cold hydrofluoric acid dissolves it readily. When heated in the air to a very high temperature, metallic zirconium burns to the oxide known as zirconia, ZrO_2, which forms either a white powder or hard lumps, according to its mode of preparation. When this compound is prepared at the lowest possible temperature, and heated to incipient redness, it glows brightly, becomes dense, and is then insoluble in the mineral acids. Zirconia is sometimes present in slight amount in the material obtained from monazite for the preparation of gas mantles, and it has been proven by experiment that the oxides of zirconium, ZrO_2, lanthanum La_2O_3 and yttrium Y_2O_3, even if present to the amount of one per cent., do not improve the lighting power of gas mantles.

Cylinders of zirconia have been employed for the Drummond light of light houses instead of those prepared from lime or magnesia, which were made to glow in the oxyhydrogen flame, and the light, thus produced, projected by means of mirrors into the distance. Zirconia possesses great radiating power and is very refractory, remaining quite unaltered after a month's use, and develops the most intense and the most fixed light under the conditions mentioned. To economize the costly material, only the outer portion of the cylinders is made of zirconia, the interior being composed of magnesia or fire clay, the two substances being firmly pressed together. Pure zirconia is prepared for this purpose by breaking up the native ores and reducing them to an impalpable powder in an agate mortar. The zirconium silicate present in the latter is then decomposed, in the presence of charcoal, by chlorine, and the zirconium and silicon chlorides separated from each other by heat, since the latter chloride is more volatile than the former. The zirconium chloride remaining is then dissolved in water and converted to oxide by precipitation with ammonia, when the hydrated zirconia thus obtained is calcined, then moistened, and submitted in moulds to the action of a press, with or without the addition of borax, boric acid or clay. The cylinders thus obtained are heated to a high temperature, by which their density and compactness is essentially increased, and are then ready for use.

Another more ready preparation of pure zirconia consists of the following operations. The zircon is first broken up, and next reduced to an impalpable powder in an agate mortar. It is then mixed with acid potassium fluoride, and the mixture fused. In this manner a perfect resolution of the mineral is easily obtained. The potassium fluor-zirconate is then separated from the insoluble fluosilicate by means of hot water, acidulated with hydrofluoric acid. From the solution thus obtained zirconia may be precipitated by ammonia.

Some of the natural compounds of zirconium, and especially the silicates, are classed on account of their size, beauty and splendor with the gems, and bring high prices, $10 a carat being a common figure. Metallic zirconium is retailed at $2.50 per gram, and the crystallized nitrate at $1 per ounce.

MINERALOGY.—The zircon bearing minerals found in nature may be subdivided into compound zircons, the gem varieties, and the altered zircons. The first mentioned division includes eudialyte, eucolite and polymignite. Of these the first two occur in Arkansas at Magnet Cove, of a rich crimson to peach blossom-red color in feldspar, and also in the syenite of Saline county, Arkansas. Eudialyte is found also in West Greenland, where it was discovered early in the century. Eucolite, a related mineral, is known to occur only in Norway. The minerals have the following characteristics: Their crystals are often tabular, or rhombohedral (eudialyte); also prismatic (eucolite), and sometimes the mineral occurs massive in embedded grains, or reniform. The cleavage in eudialyte and eucolite is nearly perfect ,their fracture subconchoidal and splintery. They are brittle, of hardness 5 to 5.5, eudialyte having a specific gravity of 2.91 to 2.93, and eucolite 3 to 3.1 Their luster is vitreous, their color verges from rose-red to bluish-red, brownish-red and chestnut-red, and their streak is uncolored. They are translucent to subtranslucent. Eudialyte from Magnet Cove analyzes as follows:

SiO_2	51.83 per cent.
Ta_2O_5	0.39 per cent.
ZrO_2	11.45 per cent.
FeO	4.37 per cent.
MnO	0.37 per cent.
CaO	14.77 per cent.
MgO	0.11 per cent.
Na_2O	13.29 per cent.
K_2O	0.43 per cent.
Cl	1.42 per cent.
Ignition	1.88 per cent.
	100.31

Specific gravity, 2.81.

Eucolite has the following composition:

SiO_2	45.15 per cent.
Ta_2O_5	3.52 per cent.
ZrO_2	12.51 per cent.
Ce_2O_3	4.80 per cent.
Y_2O_3	0.32 per cent.
FeO	3.90 per cent.
MnO	3.60 per cent.
CaO	12.11 per cent.
Na_2O	11.17 per cent.
K_2O	0.11 per cent.
Cl	0.55 per cent.
Ignition	2.11 per cent.
	99.85

Polymignite occurs at Fredriksvaern and on the island Svenoer in Norway, associated with feldspar, pyrochlore and magnetite. It is said to have been found also at Beverly, Massachusetts. In composition it is a niobate, titanate and zirconate of the cerium metals, iron and calcium. It crystallizes in slender prisms, which are vertically striated, and has a perfect conchoidal fracture, a hardness of 6.5, specific gravity 4.77 to 4.85, submetallic brilliant lustre, and a dark-brown streak. The mineral is opaque and its constituents are as follows:

Nb_2O_5	11.99 per cent.
Ta_2O_3	1.35 per cent.
ZrO_2	29.71 per cent.
TiO_2	18.90 per cent.
ThO_2	3.92 per cent.
SnO_2	0.15 per cent.
$(YEr)_2O_3$	2.26 per cent.
Ce_2O_3	5.91 per cent.
$(LaDi)_2O_3$	5.13 per cent.
Fe_2O_3	7.66 per cent.
Al_2O_3	0.19 per cent.
FeO	2,08 per cent.
MnO	1.32 per cent.
CaO	6.98 per cent.
MgO	0.16 per cent.
H_2O	0.28 per cent.
PbO	0.39 per cent.
Alkalies	1.36 per cent.
	99.74

To the gem varieties of zircon belong azorite from Sao Miguel, one of the Azores, which is colorless or pale-greenish, and occurs very seldom in sufficiently large size to serve as a gem; hyacinth, a name including the bright-colored varieties of zircon, which are sometimes large enough to be valuable as gems, and occur in Ceylon; zirconites, the gray or brownish kinds of hyacinths, and the jargons, also from Ceylon, and described under "History."

Gem zircons are found in Maine at Litchfield, at Mount Mica in Paris, Grenwood and Hebron; in Vermont at Middleburg; in Connecticut at Norwich and Haddam, in New York at Hall's mine in Moriah. Essex county, near the outlet of Two Ponds, and on Deer hill, Orange county; at Warwick, near the southern base of Mount Eve, near Amity; at Diana in Lewis county; at Hammond in St. Lawrence county, and at Johnsburg in Warren county. Further places of occurrence in the East are: Franklin and Trenton, New Jersey; Reading and Easton, Pennsylvania; the gold sands of Burke, McDowell, Polk, Rutherford and Henderson counties, North Carolina, and, in the last named county, especially the south side of the Blue Ridge, near Green river, at the Freeman mine, where zircon has been mined in large quantities for technical purposes, as mentioned under "Chemistry and Commercial Points." Zircon is also known to occur in magnetic beds of the Unaka mountains, North Carolina, some of the localities named above having furnished beautiful specimens of fine zircon, answering for gems, besides large amounts of the rough variety. In Colorado zircon is found associated with astrophylite, a compound silicate containing zirconia; at St. Peter's Dome, Pike's Peak, El Paso county, Colorado, and at Cheyenne mountain, where it occurs in brilliant reddish-brown to pink or green crystals in quartz, often surrounded with kaolinite. In California the auriferous gravel of the north fork of the American river furnished zircons, also that of Spring valley, Cherokee, Butte county, Eagle gulch and Rock Island hill, Plumas county; Picayune flat and Fresno county. Furthermore, several localities in Canada, as Grenville, Argenteuil county; St. Jerome, on the

North river, in Terrebonne county; Mille isles, where zircons are abundant and occur sometimes in very large crystals, with gigantic titanites, are known as places of occurrence; also the apatite deposits in Templeton and adjoining townships in Ottawa county, Quebec; furthermore Sebastopol township, Renfrew county, and Brudenell township of the same county, where crystals of six inches length and two or more inches thickness are found; also North Burgess, Lanark county, and Pic island, Lake Superior.

Analyses of gem zircons gave the following figures:

	From Ceylon, Colorless.	Ceylon, Yellowish.	Ceylon, Transparent.	Norway, Dark Yellow-Brown.
SiO_2	33.90	32.87	33.81	32.53
ZrO_2	64.80	64.25	66.32	64.05
Fe_2O_3	None	2.04	Trace	2.85
	98.70	99.16	100.13	99.43

Finally there is a number of rare zirconium minerals known as altered or zircon-like minerals, containing zirconia percentages, varying between 3.92 and 68.96, and associated with considerable amounts of the oxides of cerium, yttrium, erbium and uranium.

The habitat of the majority of these altered zircons is Norway, Finland, Sweden and Russia, while erytolite, which is one of them, containing from 60.78

to 66.93 per cent. ZrO_2, occurs at Rockport, Massachusetts, in granite. It has a hardness of 5 to 5.5, which is increased to 7 and 7.5 by ignition, a specific gravity of 3.98 to 4.04 and a somewhat adamantine lustre. Its color is brownish-red, and the powdered mineral has the same tint. A mineral resembling crytolite is found rather abundantly in crystalline aggregates and in massive form at Branchville, Connecticut, also in Mitchell and Henderson counties, North Carolina, further in similar condition and in large quantities in Llano county, Texas, with gadolinite and other rare species. It has a specific gravity of 3.652, but has not been analyzed. Finally a mineral from the granite of Devil's Head mountain, Douglas county, Colorado, in the Pike's Peak region, remains to be mentioned. It occurs in tapering indistinctly crystalline forms, has a brown color, a specific gravity varying between 3.60 and 3.70 and 3.64, and is described as an ill-defined zirconium mineral, allied to crytolite. Analysis shows its composition to be in one case as follows:

SiO_2	19.21 per cent.
ZrO_2	51.00 per cent.
Ce_2O_3	0.60 per cent.
Er_2O_3	4.55 per cent.
Y_2O_3	3.13 per cent.
Fe_2O_3	4.86 per cent.
MnO	9.33 per cent.
CaO	2.15 per cent.
K_2O	0.17 per cent.
Na_2O	0.42 per cent.
H_2O	12.97 per cent.
P_2O_5	0.93 per cent.
Fl	0.42 per cent.
	100.74

DETECTION.—Of all the earthy oxides ZrO_2 is the only one which remains entirely unaltered when submitted to the action of the oxyhydrogen flame, and gives out the most intense and the most fixed light. Moistened with cobalt nitrate, and intensely heated, the mass becomes of a dirty violet color. With borax zirconia yields a colorless glass, which becomes slightly opaque when cold.

QUALITATIVE DETERMINATION. — NH_4OH and $(NH_4)_2S$ produce a white flocculent precipitate of zirconium hydrate $Zr(OH)_4$, insoluble in excess, and also in NaOH or KOH. (Distinction from Al and Be.)

KOH or NaOH produce the same precipitate, insoluble in excess, not dissolved by a boiling solution of NH_4Cl. (Distinction from Be.)

$(NH_4)_2CO_3$ produces a white flocculent precipitate of basic carbonate, readily soluble in excess, and reprecipitated on boiling. (Distinction from Al.)

K_2CO_3 and Na_2CO_3 produce the same precipitate, which dissolves in a large excess of K_2CO_3, especially of $KHCO_3$. (Distinction from Al.)

$BaCO_3$ gives no precipitate in the cold, and precipitates zirconium salts imperfectly, even on boiling.

Oxalic acid gives a bulky precipitate of zirconium oxalate (distinction from Al and Be), insoluble in excess, difficultly soluble in HCl, soluble in excess of ammonium oxalate. (Distinction from Th.)

HFl produces no precipitate. (Distinction from Th and Y.)

$Na_2S_2O_3$ precipitates zirconium hyposulphite, ZrS_4O_6. (Distinction from Y, Er and Di.) The separation takes place on boiling, even in the presence of 100 parts of water to one of ZrO_2. (Distinction from Ce and La.)

Zirconium sulphate, $Zr(SO_4)_2$, forms with K_2SO_4 an insoluble double sulphate of Zr and K, insoluble in excess of K_2SO_4. (Distinction from Al and Be.) When precipitated cold, it dissolves readily in a large proportion of HCl, but is almost insoluble in water and HCl, when the K_2SO_4 is added to a hot solution. (Distinction from Th and Ce.)

Turmeric paper, when dipped into a HCl solution of a zirconium salt, acquires a brownish-red color after drying in the water bath. (Distinction from Th.)

But titanic acid, the only other metallic compound which affects turmeric paper under the same circumstances, colors the paper brown, and its presence may therefore prevent the zirconium from being recognized. If the TiO_2 be, however, first reduced by means of zinc and HCl to the state of sesquichloride—the reduction being marked in the solution by a change of color to pale-violet or blue—it no longer colors turmeric paper, and any change in the color of the latter is then due to zirconium alone. The reaction requires great care, however, as, on exposure of the paper to air the Ti_2O_3 passing again to the state of TiO_2, would in its turn color the turmeric paper, and thus render the observation doubtful.

QUANTITATIVE ESTIMATION.—Heat the zircon-bearing mineral to redness in a crucible, cast the hot mass into water, and pulverize the lumps thus obtained very finely in an agate mortar. Weigh off one gram of the fine powder, mix it with four grams of sodium carbonate and a small quantity of potassium nitrate, and heat the mixture in a platinum crucible over the blast until fused. Place the fused mass into a beaker, add water and hydrochloric acid, as usual, and a few drops of nitric acid, and evaporate to dryness to remove silica. Filter off the latter and add to the filtrate ammonia in excess, whereby zirconia, mixed with alumina and ferric oxide, are precipitated in the hydrated state. Allow to settle, filter, and dissolve the well-washed precipitate in hydrochloric acid, dilute the solution, saturate nearly with sodium carbonate, cool completely and add sodium hyposulphite (thiosulphate) to the liquid until it is entirely decolorized. Boil as long as sulphur dioxide is evolved, collect the precipitated zirconium hydrate, $Zr(OH)_4$, on a filter, wash, dry, ignite and weigh as ZrO_2. The pulverized zirconium mineral may also be decomposed by fusing it with four parts of sodium hydrate in a silver crucible.

CHAPTER XXII.

CERIUM.

HISTORY.—Cerium, one of the rare earth metals, was discovered in 1803 almost simultaneously by Klaproth, Hisinger and Berzelius, and was thus called by the latter from the asteroid Ceres, which had been discovered two years before. Klaproth isolated the base "ceria" from a Swedish mineral, known as ochroite, but identical with cerite, and named it ochroite-earth from the Greek term meaning brownish-yellow. On being informed of the discovery of Hisinger and Berzelius, and the appellation ceria chosen by them, Klaproth proposed the names "cererium" and "cererite" respectively for the element and the mineral, lest the words cerium and cerite should appear to be derived from "kera," the Greek term for wax. Subsequently he accepted, however, the names proposed by Hisinger and Berzelius.

CHEMISTRY AND COMMERCIAL POINTS.—A large number of elements are classed under the heading of "rare earths," among them being cerium, lanthanum, didymium, yttrium, ytterbium, scandium and erbium. Cerium occurs as a rule associated with lanthanum and didymium in nature, and it may be said, that either of these bodies is usually found in minerals, combined with a number of other elements of the same group. Four of them, namely cerium, lanthanum, scandium and ytterbium, have been thoroughly investigated, and their atomic weights determined, but the latest researches show that yttrium, didymium and erbium are to be considered as complex bodies. These three elements will, therefore, find but scant attention in the following lines, since spectrum analysis has proven that yttrium consists of not less than five distinct metals, didymium of nine or ten, and erbium of two different bodies. The same consideration holds good for another series of rare earth metals, known as holmium, mosandrium, thulium and samarium, which were obtained by a number of fractionations, holmium and mosandrium having been shown to be mixtures of two substances, and thulium and samarium to be of similar character. Whether these constituents can be further subdivided has still to be determined.

The most important earth metal of the class is cerium of the atomic weight 140.2 and specific gravity 6.72. It may be obtained in the metallic condition by the electrolysis of the fused chloride, and represents then a body resembling iron in color and lustre, which fuses at about 950° C. It is ductile and malleable, oxidizes in moist air, and slowly decomposes water with the formation of the hydroxide and the generation of hydrogen. If heated in air it burns with greater brilliancy than magnesium, and it combines directly with the halogens.

The importance of cerium compounds in the manufacture of Welsbach's mantles was pointed out under "thorium," but cerium salts have also found application in a number of other commercial pursuits. Among the latter is the utilization of cerium sulphate of the formula $Ce_2(SO_4)_3$ for the development of aniline black, its effect being said to be superior to that of the vanadium preparation. As the presence of the several metals associated with the mineral cerite—which is virtually a silicate of cerium, didymium and lanthanum, and serves for the production of the majority of cerium salts—does not interfere with the application of the crude solution, obtained from it for the dyeing process, one kilo of the finely powdered mineral is treated with its own weight of concentrated sulphuric acid and digested at a gentle heat with occasional stirring. Much heat is developed, and a portion of the acid volatilized thereby, so that at the end of the operation a dry gray mass remains, which is powdered, mixed with 250 to 300 grams concentrated sulphuric acid, digested at a gentle heat for some days and the acid expelled by heating on a sand bath. The resulting gray powder is cast in small portions into cold water, under constant agitation and frequent addition of ice, to keep down the temperature, the mixture digested with occasional stirring for a day or two, and the liquid decanted, when the residue is again treated with water to remove all soluble constituents. One kilo of cerite produces about twenty liters of solution, which may be used directly or evaporated, and the clear rose-colored crystals, separating from the liquid, dissolved in cold water. Of this solution ten cubic centimeters, containing about one-third gram of cerium sesquioxide, is sufficient to develop over 110 liters of the printing solution, containing over six kilos of the aniline salt. The cloth being printed is aged at 38° to 43° C. for about eight hours, when the deep blue-black color characteristic of the cerium salt is developed in a weak aniline bath.

Many of the organic cerous salts have found application in medicine, the oxalate having proved a useful sedative in cases of hysteria, while it is said to be a good specific against seasickness. Other salts of cerium, like the double citrates, tartrates and lactates of cerium, potassium, sodium and ammonium, are also used medicinally.

Metallic cerium in powder form is retailed at $4 per gram, the nitrate at 35 cents per ounce and the oxalate at 90 cents per pound.

MINERALOGY.—One of the principal cerium minerals is cerite, whose habitat is Bastnaes in Sweden, where it forms beds in gneiss and is associated with mica, hornblende and chalcopyrite. It bears considerable resemblance to the red granular variety of corundum, but is readily distinguished from it by its inferior hardness, that of corundum being 9 and that of cerite 5.5. The mineral is rarely found crystallized, and if so, in prismatic forms, is brittle and slightly translucent, has a splintery fracture and a specific gravity varying between 4.86 and 4.912, and an adamantine or resinous lüstre. Its color verges from clove-brown and cherry-red to gray, and its streak is grayish-white. In composition it is a hydrated silicate of cerium, didymium and lanthanum, with admixtures of small amounts of iron, lime and occasionally alumina, as becomes apparent from the following analytical data:

	I.	II.
SiO_2	22.79	19.18 per cent.
Ce_2O_3	24.06	64.55 per cent.
$\left.\begin{matrix}Di_2O_3\\La_2O_3\end{matrix}\right\}$	35.37	7.28 per cent.
FeO	3.92	1.54 per cent.
Al_2O_3	1.26	None
CaO	4.35	1.35 per cent.
H_2O	3.44	5.71 per cent.
Gangue	4.33	None
	99.52	99.61

Specific gravity of II., 4.86.

Cerite gives off water when heated in a test tube, and is infusible in the blowpipe flame. When heated in the oxidizing or outer flame, it forms a yellow globule, which becomes almost colorless on cooling; in the reducing or inner flame it shows a weak iron reaction. With soda it fuses in the flame to a dark yellow, slaggy mass, but does not dissolve, and forms a gelatinous body, when treated with hydrochloric acid.

A second mineral, to be considered under this head, is orthite, also known as allanite, which occurs in Greenland in granite; at Criffel, Scotland, in small crystals: at Jotun Fjeld, Norway, in a kind of porphyry, and at Snarum, Norway, in albite, along with rutile and apatite. In the United States it is found in Massachusetts at the Bolton quarry, at S. Royalton in boulders, in Athol, on the road to Westminster in gneiss, and at Swampscot, near Marblehead; also in Connecticut at Allen's vein, in the gneiss quarries, Haddam; in New York near West Point in tabular crystals; at Moriah, Essex county, with magnetite and apatite, some of the crystals being eight to ten inches long, six to eight broad and one to two inches thick, and at Monroe in Orange county. In New Jersey it is met with at Franklin with feldspar and magnetite; in Pennsylvania at South Mountain, near Bethlehem, in large crystals; at East Bradford in Chester county, and in abundance at Priceton, near Reading, Berks county. In Virginia orthite occurs in large masses in Amherst county, and also in Beldford, Nelson and Amelia counties; in North Carolina in crystals at the hiddenite mine in Alexander county with emerald, also in Mitchell county at the Wiseman mica mine, at Balsam Gap, Buncombe county, and massive in large quantities near Bethany Church, Iredell county, also at Democrat Post Office, Madison county, and at Brindletown and the zircon mines in Henderson county. In Colorado it is found at Devil's Head mountain. Douglas county, and as an accessory rock constituent in many localities. In Canada it occurs at Bay St. Paul, Charlevoix county, Quebec; in a rock composed of labradorite (an aluminum, calcium, sodium silicate), and hypersthene (a silicate of magnesia, iron, alumina and lime) from Lake St. John, Chicoutimi county, Quebec, and at Hollow lake, headwaters of the South Muskoka, Ontario. The variety from Douglas county, Colorado, and that from Amelia county, Virginia, analyze as follows:

	Amelia County, Virginia.	Douglas County, Colorado.
SiO_2	32.35	31.13 per cent.
ThO_2	None	0.21 per cent.
Al_2O_3	16.42	11.44 per cent.
Fe_2O_3	4.49	6.24 per cent.
Ce_2O_3	11.14	12.50 per cent.
Di_2O_3	6.91	10.98 per cent.
La_2O_3	3.47	
Y_2O_3	None	None
Er_2O_3	None	0.27 (BeO)pc.
FeO	10.48	13.59 per cent.
MnO	1.12	0.61 per cent.
CaO	11.47	9.44 per cent.
MgO	None	0.16 per cent.
K_2O	0.46	Trace per cent.
Na_2O		
H_2O	2.31	2.78 per cent.
	100.62	99.91

Specific gravity: Virginia mineral, 3.323; Colorado mineral, 3.520.

All kinds and varieties of orthite yield water, when being strongly heated in a closed tube, fuse easily before the blowpipe and swell up to a dark, blebby, magnetic glass. They give the reactions for iron with fluxes, and most of them form a gelatine, when treated with hydrochloric acid, but they are not decomposed by acids, if ignited previously. Orthite is often found crystallized in flat tabular forms, or in long, slender and sometimes acicular prismatic crystals, also massive and in embedded angular or rounded grains. Its fracture is uneven or sub-conchoidal, its hardness 5.5 to 6, and its specific gravity 3.5 to 4.2. It is brittle, of a color varying between pitch-brown and black, or brownish, greenish, grayish or yellowish, with a submetallic, pitchy or resinous and sometimes vitreous lustre. The mineral is subtranslucent to opaque, and its streak mostly gray, but sometimes slightly greenish or brownish.

A third cerium bearing mineral, known as gadolinite, and thus named from the Swedish chemist Gadolin, who discovered the presence of a new oxide, yttria, in it as early as 1794, occurs at Ytterby, near Stockholm, and in a number of localities in Sweden and Norway, but also in Llano county, Texas, on the west bank of the Colorado river, five miles south of Bluffton. It is found at the latter place in nodular masses and rough crystals, sometimes forty to sixty pounds in weight, but averaging generally but half a pound. Gadolinite occurs also at Devil's Head mountain, Douglas county, Colorado. Analyses of the Colorado and Texas varieties gave the following data:

	Douglas County, Colorado.	Llano County, Texas.
SiO_2	22.13	23.79 per cent.
ThO_2	0.89	0.58 per cent.
Y_2O_3	22.24	41.55 per cent.
Ce_2O_3	11.10	2.62 per cent.
$(DiLa)_2O_3$	21.23	5.22 per cent.
Fe_2O_3	3.47	0.96 per cent.
FeO	10.43	12.42 per cent.
BeO	7.19	11.33 per cent.
CaO	0.48	0.74 per cent.
Na_2O	0.46	Trace per cent.
H_2O	0.86	1.03 per cent.
P_2O_5	None	0.05 per cent.
	100.48	100.29

Specific gravity: Colorado mineral, 4.560; Texas mineral, 4.239.

Besides these three cerium minerals there are woehlerite, fergusonite, euxenite, thorite, samarskite and columbite, most of which have been described before. The first of them has been named from the distinguished chemist, Frederic Woehler. Its habitat is a number of islands in the Langesund fiord, near Brevik, in Norway, none of the mineral having been discovered so far in the United States. It has a color ranging between light-yellow, wine-honey, resin-yellow, brownish and grayish, is brittle, conchoidal to splintery in fracture, of hardness 5.5 to 6, and specific gravity 3.41 to 3.44. Its lustre is vitreous, inclining to resinous, its appearance transparent to subtranslucent, and its streak yellowish-white. In a strong heat of the blowpipe it fuses to a yellowish glass, and gives with fluxes the reactions of manganese, iron and silica. It dissolves easily, when heated with hydrochloric acid, silica and niobium pentoxide separating out. The composition of woehlerite is given by the following data:

SiO_2	30.12	per cent.
ZrO_2	16.11	per cent.
TiO_2	0.42	per cent.
Nb_2O_5	12.85	per cent.
Fe_2O_3	0.48	per cent.
FeO	1.26	per cent.
MnO	1.00	per cent.
CaO	26.95	per cent.
MgO	0.12	per cent.
Na_2O	7.50	per cent.
H_2O	0.74	per cent.
Fl	2.98	per cent.
Ce_2O_3	0.66	per cent.
	101.19	

Specific gravity, 3.442.

The rare earths are also found in small quantities, and usually associated with calcium, in the ashes of plants, and in boneash, various limestones, apatites and scheelites.

Detection.—All cerium compounds give with borax or microcosmic salt in the outer flame a clear bead, which is dark-red while hot (distinction from the other earths), fainter or nearly colorless on cooling. In the inner flame, a colorless bead, or if ceric oxide is present, a yellow opaque bead is obtained. Lanthanum compounds give colorless beads, and didymium compounds give with borax colorless, or, if in large quantity, pale rose-colored beads, in both flames, and with microcosmic salt, in the reducing flame, an amethyst-red bead, inclining to violet.

QUALITATIVE DETERMINATION. — Cerous compounds, like the chloride, give with $(NH_4)_2S$ a precipitate of white cerous hydrate, insoluble in excess. Cerous chloride is not volatile. (Distinction from Al, Be and Zr.) Cerous sulphate is not entirely soluble in boiling water.

NH_4OH precipitates a basic salt, insoluble in excess, the presence of tartaric acid prevents the precipitation by ammonia (distinction from Y), but not by KOH. KOH or NaOH precipitate white cerous hydrate, insoluble in excess, which turns yellow on exposure to the air, or when acted upon by oxidizing agents, such as chlorine water, sodium hypochlorite, etc., being converted into the yellow hydrated cerous-ceric oxide Ce_2O_4 $3H_2O$. (Distinction from Al and Be.)

K_2CO_3, Na_2CO_3 or $(NH_4)_2CO_3$ produce a white precipitate of cerous carbonate, $Ce_2(CO_3)_3$ sparingly soluble in excess of the fixed carbonates, somewhat more soluble in $(NH_4)_2CO_3$; insoluble in water and CO_2; decomposed by dilute acids. $BaCO_3$ precipitates cerium salts slowly, but completely on standing.

Oxalic acid or ammonium oxalate precipitate cerium compounds completely, even from moderately acid solutions as a curdy white precipitate (turning slowly crystalline) of cerous oxalate $Ce(C_2O_4)_3\ 9H_2O$, insoluble in excess of the reagents (precipitants); (distinction from Zr) but soluble in a large excess of HCl. On ignition cerous oxalate leaves yellowish-white cerous-ceric oxide Ce_3O_4 or CeO_2. (Distinction from Al and Be, which form soluble oxalates.)

A saturated solution of potassium sulphate produces a white crystalline precipitate of potassium cerous sulphate $Ce_2(SO_4)_3\ 3K_2SO_4+H_2O$ even from somewhat acid solutions. (Distinction from Al and Be), difficultly soluble in cold water, readily soluble on heating, quite insoluble in a saturated solution of K_2SO_4 (distinction from Y and Er), soluble in much dilute HCl. With dilute solutions the precipitate takes some time to form. This characteristic precipitate, as well as the easily distinguished oxalate, and the yellow precipitate of cerous-ceric oxide—free from La and Di, precipitable in the filtrate as oxalates—which oxidizing agents produce, serve to distinguish cerium from all other metals.

CERIC COMPOUNDS.—Salts of CeO_2, such as the sulphate and oxalate are yellow, and are either difficultly soluble or insoluble in water. When CeO_2 is heated with HCl it does not form $CeCl_4$, but yields $(CeCl_3)_2+Cl_2$. Oxidizing agents, such as Cl, passed into a solution of KOH containing $Ce_2(OH)_6$ in suspension; sodium hypo-chlorite, PbO_2, HNO_3, HgO, or potassium permanganate, convert cerous into ceric compounds, and furnish methods for the separation of Ce from La and Di. Reducing agents produce the reverse chemical action. Cerium resembles in this respect iron rather than aluminum.

QUANTITATIVE ESTIMATION.—In case the separation of Ce from La and Di is intended, a convenient method consists of treating the cerous salts with PbO_2 and dilute HNO_3, when the solution turns yellow, even if only small quantities of cerium be present. By evaporating the yellowish solution to dryness and heating sufficiently to drive off part of the HNO_3, so as to form a basic ceric nitrate, insoluble in water or dilute HNO_3, lanthanum and didymium can be dissolved out as nitrates. After removing the lead nitrate from the solution by H_2S, the La and Di are precipitated as oxalates. The residuary basic ceric nitrate is dissolved in fuming HNO_3, and lead removed by H_2S, and the cerium precipitated as oxalate.

The minerals carrying rare earths are as a rule silicates, phosphates, niobates, or tantalates of the earths, accompanied by the more common bases, such as oxides of iron, calcium, aluminum, manganese and others.

The most important primary point, assuring success, when analyzing these earths is the reduction of the mineral to a very finely pulverized and impalpable powder, by grinding it first on the bucking board, then passing it through a hundred and twenty mesh sieve, then rubbing it down in a Wedgewood mortar, and finally working it in an agate mortar, so as to facilitate its decomposition by acids. One, two or five grams of the mineral having been weighed off, the pulverized mass should be covered with hydrochloric acid in a casserole, and the mixture heated to boiling, and ebullition continued, under frequent addition of fresh portions of the acid, until the mineral is entirely decomposed, which condition can be ascertained by examining the appearance of the silica usually remaining, which should be white. The earths and oxides, thus brought into solution, are now present as chlorides, and the liquid should be evaporated as usual to separate silica.

Minerals of the rare earths are in cases, however, not decomposable by hydrochloric acid, and in such an emergency the ore should be heated with an excess of concentrated sulphuric acid, and the excess of acid driven off until voluminous vapors of the anhydride SO_3 appear. The mass is finally reduced to dryness, and the residue dropped in small portions and with occasional stirring into a beaker, half filled with distilled water, and surrounded by pieces of ice. The mixture is then allowed to stand for half an hour, when the sulphates of the rare earths and of some of the other bases present will have been dissolved.

Some minerals, containing rare earths, cannot be decomposed even by sulphuric acid, and must be fused, therefore, with an excess of acid sodium sulphate. The fused mass thus obtained is allowed to cool, and then introduced into iced water, as described above.

In this manner there results a solution of acid reaction, containing either the chlorides or sulphates of the bases, which is separated from the residue by filtration. To the filtrate is added a saturated solution of oxalic acid in excess, when the oxalates of the rare earths, together with small amounts of iron, lime, etc., are precipitated. The oxalates are allowed to settle, the supernatant liquid is drawn off, and the precipitate washed by decantation with hot water containing one per cent. of hydrochloric acid, until the wash water gives no reaction for iron. The oxalates are then brought upon a filter, dried and ignited. The resulting oxides are dissolved by heating them with concentrated nitric acid, when the solution is diluted and treated with ammonia. The precipitated hydroxides are washed by decantation with water, and then dissolved in hydrochloric acid. Hydrogen sulphide is passed through a portion of this solution, and if a precipitate results, the whole of the solution is treated with the gas. The precipitated sulphides are filtered off, the filtrate is freed from hydrogen sulphide either by heat or by blowing carbon dioxide or air through the liquid, and any sulphur that may have separated is removed by filtration. The clear solution thus obtained contains the rare earths practically free from other elements.

CHAPTER XXIII.

LANTHANUM.

HISTORY.—Lanthanum, which received its name from the Greek term meaning "to be concealed," was discovered and thus named by Mosander about 1820.

OTHER POINTS.—Lanthanum has not found any commercial application unto the present. It is known to be present in cerite, and its separation from the other rare earths is a most laborious process, the amount of the earth obtainable in anything like a pure state being very small in comparison to the mass of material worked. When separating its compounds, reference must be had, therefore, to publications of specialists.

The metal itself has the atomic weight 138.2, and a specific gravity 6.16, and resembles iron in color and lustre, oxidizes in the air and burns, when introduced into a flame, with a bright light. It is usually prepared by electrolyzing the chloride.

QUALITATIVE DETERMINATION.—This metal forms only ous-salts, which are colorless, when free from didymium salts, and possess a sweet astringent taste. Lanthanic oxide is white, and is not altered, even by strong ignition (distinction from Ce), being still readily soluble in acids. Both the oxide and the hydrate turn red litmus paper blue. It decomposes ammonium salts, in solution, on boiling, with evolution of NH_3. Lanthanum resembles in this respect magnesium. A solution of lanthanum sulphate, saturated in the cold, deposits a portion of the salt at 30° C. (Distinction from Ce.) In its reactions lanthanum resembles closely cerium.

NH_4OH and $(NH_4)_2S$ precipitate basic salts, which pass milky through the filter on washing.

KOH or NaOH precipitate lanthanum hydrate $La_2(OH)_6$ insoluble in excess, unalterable in the air, or in the presence of oxidizing agents. (Distinction from Ce.)

$(NH_4)_2CO_3$ gives a precipitate which is insoluble in an excess of the reagent. (Distinction from Ce.)

K_2CO_3, Na_2CO_3, $BaCO_3$, oxalic acid or potassium sulphate give similar precipitates as with cerium salts.

When the slimy precipitate, which a cold dilute solution of lanthanum oxide yields on supersaturation with NH_4OH, is washed repeatedly with cold water, and a few small crystals of iodine are added to it, a blue coloration is produced, which gradually pervades the entire mixture. (Characteristic for lanthanum only.)

CHAPTER XXIV.

YTTERBIUM.

HISTORY.—Ytterbium was discovered by Marignac in 1878 when investigating closely the minerals gadolinite and euxenite. He named the oxide "ytterbia" from Ytterby, Sweden, the place of occurrence of the minerals.

CHEMISTRY AND COMMERCIAL POINTS.—The atomic weight of ytterbium is 173. Euxenite is the most abundant source of this earth metal, where it is accompanied by the oxides of six or seven closely related elements, as scandium, thallium and others. Ytterbia has been separated by the very tedious process of evaporating the nitrates, and heating considerably, whereby basic salts insoluble in water are formed, Sc, Th, Di, Er and Y being relatively less soluble than ytterbium. The pure earth is obtained from the nitrate by addition of oxalic acid and igniting the oxalate. No commercial use has been established for this element or its compounds.

The mineralogical points referring to ytterbium have been given before. Its detection is best accomplished by spectrum analysis.

QUALITATIVE DETERMINATION.—Yb_2O_3 is a heavy white difficultly fusible powder, easily soluble in warm dilute acids. The solutions are colorless. Specific gravity of oxide, 9.175. Its salts have a sweet taste. The nitrate is scarcely decomposed by heating, and remains soluble. (Characteristic.) NH_4OH precipitates the hydrate $Yb_2(OH)_6$. The sulphate $Yb_2(SO_4)_3$ is soluble in water. The acid selenite $Yb_2(SeO_3)_3\ H_2SeO_3\ 4H_2O$, precipitated from neutral solutions, is white and insoluble. The oxalate $Yb(C_2O_4)_3\ 10H_2O$ is insoluble in dilute acids.

QUANTITATIVE ESTIMATION is effected according to the points given above.

CHAPTER XXV.

SCANDIUM.

HISTORY.—A special interest attaches to scandium, since its existence was deduced theoretically by the Russian chemist Mendeleef from the periodic system of the elements. He named it ekaboron, and as the "scandium" discovered by Nilson in 1879 during the separation of some of the rare earths showed exactly the properties predicted by Mendeleef, the discovery of Nilson formed a further confirmation of the reliability of the Russian's method. Thus the atomic weight of the metal was found to be 44, and to fill the gap between calcium and titanium. It is, therefore, found in the third group of the table of the periodic system, which is headed by boron and aluminum. Scandium was named thus by Nilson in honor of his country, the Scandinavian peninsula, where the minerals containing the earth were originally found.

The metal or its compounds have no commercial importance.

MINERALOGY.—Scandium occurs in the minerals euxenite, gadolinite and keilhauite or yttrotitanite, but in such small quantities that they are usually not determined in ordinary analyses. Thus in one case four kilos of gadolinite furnished only 0.8 gram of scandium oxide, and 3 kilos keilhauite 1.2 grams of the base. The latter mineral was named after Professor Keilhau of Norway. The habitat of these minerals is Arendal and Snarum, Norway, and the islands Buoe, Askeroe, Alve and Narestoe, where they occur in feldspathic rock, in crystals weighing sometimes two and a half pounds, and in masses of fifteen to twenty pounds. They are to be considered as titano-silicates of the yttrium metals, and of calcium, aluminum and ferric iron. Keilhauite has a quite distinct cleavage, a hardness of 6.5, and a specific gravity of 3.52 to 3.77. Its lustre is vitreous to resinous, its color in most cases brownish-black, which appears brownish-red and translucent in splinters, but also dull-brown and pale grayish-brown in some specimens. Its streak verges between grayish-brown and pale dirty-yellow.

Before the blowpipe the mineral fuses with intumescence easily to a black shining glass, and yields an iron-colored glass with borax, which becomes blood-red in the inner flame. With salt of phosphorus it gives the iron reaction and a silica skeleton, and in the inner flame a violet bead. It is decomposed by hydrochloric acid. The detection of the element scandium may be accomplished by spectrum analysis.

QUALITATIVE DETERMINATION.—Scandium has the atomic weight 44.1. The earth concentrates in the insoluble basic nitrates on the separation of Yb. Its nitrate is next to Yb in difficulty of decomposition by heat, the two earths differing greatly in this respect from Er, Tb, Y and others. Yb and Sc may be separated by heating their nitrates, or by precipitation of scandium potassium sulphate by addition of K_2SO_4. $Sc_2(SO_4)_3\ 3K_2SO_4$ is quite insoluble, the Yb salt is soluble, however. Sc_2O_3 is white, of specific gravity 3.864, and resembles MgO or BaO; it is difficultly fusible, and is not very soluble in acids. NH_4OH precipitates $Sc_2(OH)_6$, insoluble in excess of KOH or NH_4OH. The oxalate is slightly soluble in water (1 in 1080). Other salts are very similar to those of Yb.

Quantitative Estimation.—Exact quantitative methods for the separation of some of the rare earths are not yet known.

CHAPTER XXVI.

TITANIUM.

HISTORY.—Titanium was discovered in 1791 by Gregor, an English priest, when investigating a peculiar mineral occurring in form of a black sand, to which he gave the name menachanite (menaccanite) from its place of occurrence, Menachan in Cornwall. The element present in the compound he called "menachin." In 1794 Klaproth recognized a peculiar oxide in rutile, whose element he called "titanium," and which was later found to be identical with the menachin of Gregor. This name titanium is derived from the term "titans," the fabled giants of ancient mythology, hence indicating enormous in size or strength. It has been universally accepted. Berzelius, Woehler and Rose have contributed extensively to the further knowledge of titanium compounds and derivatives.

CHEMISTRY AND COMMERCIAL POINTS.—Titanium of atomic weight 48.1 is a gray metallic powder, having the color and lustre of iron, which burns with great splendor, when heated in the air, and decomposes water on boiling. When heated to redness in oxygen gas it burns with a vivid light resembling a discharge of electricity. It dissolves in dilute hydrochloric and sulphuric acids with brisk evolution of hydrogen. The metal is usually prepared by heating potassium titano-fluoride of the formula K_2TiFl_6 with potassium in a covered crucible. The metal is then set free with vivid incandescence, and the potassium fluoride formed may be removed by washing with water.

Metallic titanium may also be prepared by passing the vapor of the tetrachloride through a heated bulb-tube containing lumps of sodium, separating the resulting mixture of salt and titanium with cold water, washing the residual titanium with ether, and drying it over sulphuric acid. When thus prepared it does not act upon water at any temperature below 500° C.

The presence of titanium in iron ores and in the pig-iron or steel prepared therefrom, is generally regarded as injurious. Opinions in this regard are, however, divergent, since recent experiments seem to indicate that certain percentages of titanium in steel or iron are rather beneficial. The several titaniferous ores as well as the metal titanium and ferrotitanium are, therefore, liable to become prominent in the near future.

The ferrocyanide of titanium has found application in commerce on account of its fine green color. It is prepared by adding potassium ferrocyanide to a solution of hydrated titanic oxide in hydrochloric acid, and washing and drying the green colored powder. When in this condition it forms a substitute for the poisonous Schweinfurth green and other arsenical pigments.

MINERALOGY.—The mineral rutile, when pure, consisting of titanium dioxide, in the proportion of—

Ti	60.0 per cent.
O	40.0 per cent.
	100.0

is usually accompanied in nature by iron, the percentages of the latter amounting sometimes to ten per cent. The form of crystallization is usually prismatic, the crystals being striated vertically or furrowed, also frequently slender and acicular, but rarely compact and massive. Their cleavage is distinct, their fracture subconchoidal to uneven, with a hardness of 6 to 6.5, and a specific gravity of 4.18 to 4.25. Rutile is brittle, of metallic adamantine lustre, of a reddish-brown color passing into red, with varying tints of yellow, blue, violet, black and rarely grass green. By transmitted light the mineral appears deep red, is transparent to opaque, and shows a pale brown streak. The ordinary variety is brownish-red, and has a specific gravity of 4.18 to 4.25, others being edisonite, named after the inventor, Thomas A. Edison, which occurs very sparingly in the gold washings of Polk county, North Carolina, and nigrine, a ferriferous rutile of black color on account of its contents in ferric iron, which amount to two or three per cent. A jet black rutile is found at St. Peter's Dome, Colorado, which contains 3.77 per cent ferrous iron, and has a specific gravity of 4.288. A black rutile occurs furthermore in the granite of the Black Hills, Dakota, in twin crystals, prismatic and orthorombic in habit, which has a specific gravity of 5.29 to 5.31, and contains 8.01 per cent. FeO and 1.35 per cent. SnO_2. Finally there exists a grass green variety, colored by chrome.

Rutile is infusible before the blowpipe and gives with salt of phosphorus a colorless bead, which assumes in the reducing flame a violet color on cooling. Most varieties contain iron, and give a brownish-yellow or red bead in the reducing flame, the violet only appearing after treatment of the bead with metallic tin or charcoal. It is insoluble in acids, and made soluble by fusion with an alkali or alkaline carbonate. The solution containing an excess of acid, with the addition of tin foil, gives a beautiful violet color when concentrated.

Rutile occurs in granite, gneiss, mica slate and syenitic rock, and sometimes in granular limestone and dolomite, and is common, as a secondary product, in many slates in the form of microlites. It is generally found in embedded crystals, often in masses of quartz or feldspar, and frequently in acicular crystals penetrating quartz, also in phlogopite, a magnesium mica, and has been observed in diamond. It has also been met with in hematite and ilmenite, an iron titanate, but rarely in chromite of the formula Cr_2O_3. FeO. It is common in grains in many auriferous sands.

Not considering foreign localities, its occurrence has been observed at Warren, Maine; at Lyme and

Hanover, New Hampshire; at Waterbury, Bristol, Dummerston and Putney, Vermont; at Barre, Windsor, Shelburne, Leyden and Conway, Massachusetts; at North Guilford, at Lane's mine, Monroe, and the adjoining town of Huntingdon, Connecticut; at Edenville, Warwick, Amity and Kingsbridge, New York; at Sudsbury, Parksburg, West Bradford, Newlin, Pennsylvania; at Newton, New Jersey; at Crowder's Mountain, Stony Point, North Carolina; in Habersham county and at Graves' mountain in Georgia· and at Magnet Cove, Arkansas. It is of frequent occurrence in Colorado, beautiful specimens of the black variety, and resembling twins of cassiterite, having been found.

Another titanium mineral, crystallizing in octahedra, is octahedrite or anatase, which has the same composition as rutile, and behaves in the same manner before the blowpipe as the latter. Its cleavage is perfect, its fracture subconchoidal, its hardness 5.5 to 6, and its specific gravity 3.82 to 3.95, and sometimes 4.11 to 4.16 after being heated. It is brittle, has an adamantine lustre, various shades as brown, passing into indigo blue, and black, and appears greenish-yellow by transmitted light. The mineral is transparent to nearly opaque, and gives an uncolored streak. It occurs in the United States at the Dexter lime rock, Smithfield, Rhode Island, in dolomite, and in the washings at Brindletown, Burke county, North Carolina, in transparent tabular crystals.

Brookite, a third titanium mineral of the same composition as rutile and octahedrite, is found only in crystals. Its habit is varied, often tabular, or prismatic, and striated vertically, sometimes simulating rutile. Its cleavage is indistinct, its fracture subconchoidal to uneven, and it has a hardness of 5.5 to 6 with a specific gravity of 3.87 to 4.01. The mineral is brittle, its lustre metallic adamantine to submetallic, its color hair brown, yellowish, reddish, reddish-brown, also brown to iron-black, and it is translucent. Its streak is uncolored or verges into grayish and yellowish. Before the blowpipe it behaves like rutile. Brookite, which was named after the English crystallographer and mineralogist, H. J. Brooke, occurs in the United States at Magnet Cove, Ozark mountains, Arkansas, in thick black crystals, in small crystals in the gold washings of North Carolina, at the lead mine of Ellenville, Ulster county, New York, and at Paris, Maine.

Perovskite, virtually a calcium titanate, deserves mention under this head. It is named after von Perovski of St. Petersburg, and carries, when pure,

TiO_2	58.9 per cent.
CaO	41.1 per cent.
	100.0

The mineral is found in the United States in serpentine at Syracuse, New York, and also in Elliott county, Kentucky. Its crystals are generally cubic in habit, but are often highly modified; its cleavage is rather perfect, its fracture uneven to subconchoidal, its hardness 5.5, and its specific gravity 4.017. It is brittle, of adamantine lustre, and its color varies from pale-yellow to honey-yellow, orange-yellow, reddish-brown to grayish-black. Perovskite is transparent to opaque in appearance, and has either a colorless or grayish streak. It is infusible on charcoal, dissolves easily in the oxidizing flame with salt of phosphorus, and gives a greenish bead while hot, which becomes colorless on cooling; in the reducing flame the bead changes to grayish-green, and on cooling assumes a violet-blue tint. It is entirely decomposed by boiling sulphuric acid. Specimens of perovskite analyzed as follows:

	I.	II.	
TiO_2.....	59.00	58.66	per cent.
CaO......	36.76	41.47	per cent.
FeO......	4.79	None	
MgO MnO...	0.11	None	
	100.66	100.13	

Finally, ilmenite, also known as menaccanite, an iron titanate, remains to be mentioned. It consists, when pure, of

TiO_2................	52.7 per cent.
FeO	47.3 per cent.
	100.0

Its crystals are usually thick and tabular, also acute rhombohedral, but occur often in thin plates or laminae. The mineral is found, however, also in massive and compact form, in embedded grains, and loose as sand. Its fracture is conchoidal, its hardness 5 to 6, its specific gravity 4.5 to 5, and its lustre submetallic. Ilmenite is opaque, has an iron-black color, a submetallic streak, and its streak-powder varies in color from black to brownish-red. It affects slightly the magnetic needle.

Before the blowpipe the mineral is infusible in the outer flame, but is slightly rounded on the edges in the inner flame. With borax and salt of phosphorus it reacts for iron in the outer flame, and with the latter flux assumes a more or less intense brownish-red color in the inner flame. If this is treated with tin on charcoal, it changes to a violet-red color, when the amount of tianium is not too small. The pulverized mineral, heated with hydrochloric acid, is slowly dissolved to a yellow solution, which, filtered from the undecomposed mineral and boiled with the addition of tin-foil, assumes a beautiful blue or violet color. It is decomposed by fusion with acid sulphate of sodium or potassium.

Ilmenite occurs in Warwick, Amity and Monroe, Orange county, New York; also four miles west of Edenville, and near Greenwood furnace, and at Chester and South Royalston, Massachusetts; at Litchfield, Connecticut, and Troy, Vermont. Carter's mine, North Carolina, is also known as a place of occurrence.

Vast deposits or beds of titanic ore are found at Bay St. Paul, in Quebec, Canada, and grains occur in the gold sand of California. The composition of ilmenite becomes clear from the following analytical data:

	Ilmenite from Ilmen Mountains.	Washingtonite from Litchfield, Conn.
TiO_2	45.93	22.21 per cent.
Fe_2O_3	14.30	59.07 per cent.
FeO	36.52	18.72 per cent.
MnO	2.72	None
MgO	0.59	None
	100.06	100.00

Specific gravity of Ilmenite, 4.811 to 4.873.

Specific gravity of Washingtonite, 4.992.

Titanium is often present in slags and pig-iron, also in mineral waters and in the sun's atmosphere. Its presence in clays in the form of oxide reduces their refractibility considerably.

DETECTION OF TITANIUM.—Dissolve the finely pulverized titaniferous mineral in hydrochloric or nitric acid, evaporate to dryness, take up with dilute acid and water, filter, and add hydrogen peroxide to the filtrate, when a fine yellow or orange color appears. Ferric chloride should not be present, hence pass a current of sulphur dioxide through the liquid to reduce it to the ferrous state.

QUALITATIVE DETERMINATION. — Titanium compounds, when heated on charcoal before the blowpipe, are not reduced to the metallic state. (Distinction from In.) Heated in a borax bead on charcoal, or better still, in a bead of microcosmic salt, pure TiO_2, or a titanate containing bases, which do not themselves color the borax bead, yield in the outer flame a colorless glass, but in the inner flame, a glass which is yellow while hot, but assumes a violet color on cooling. The reduction is promoted by the addition of a little zinc or tin. If some $FeSO_4$ be added, the bead obtained in the inner flame becomes blood-red.

NH_4OH, $(NH_4)_2S$, KOH or NaOH, alkaline carbonates, as well as $BaCO_3$ produce a bulky white precipitate of ortho-titanic hydrate H_2TiO_3 or $TiO(OH)_2$, which is insoluble in an excess of the precipitants. When thrown down in the cold and washed with cold water, it is readily soluble in dilute HCl or in dilute H_2SO_4. Washing with hot water converts it into insoluble metatitanium hydrate. The presence of tartaric acid prevents the precipitation. (Iron as well as Ni, Co, Zn and U are precipitated by $(NH_4)_2S$ in the presence of tartaric acid and NH_4OH, while Mn is not, and these may therefore be separated thus from Ti.)

Infusion of galls produces a brownish precipitate, which speedily turns orange-red.

Na_2HPO_4 throws down the titanic acid almost completely from an acid solution as a white gelatinous phosphate, which, when washed and dried, leaves a basic salt $Ti(OH)PO_4\ H_2O$.

Metallic tin or zinc, immersed in a HCl solution of TiO_2, evolves hydrogen, and reduces the TiO_2 to

Ti_2O_3, which gives rise to a pale violet or blue coloration, and finally throws down a dark violet precipitate, which is rapidly reoxidized to white TiO_2 with decomposition of the water, or when exposed to the air. This reaction frequently reveals the presence of TiO_2 in the analysis of iron ores during the process of reduction with zinc, previous to the estimation of iron by potassium permanganate.

The metal titanium has a great affinity for nitrogen, with which it combines directly. Hence its occurrence in blast furnace slags as nitride $TiCy_2$ $3Ti_3N_2$ in bright copper-colored cubes.

QUANTITATIVE ESTIMATION.—In order to determine titanic anhydride TiO_2, the finely powdered mineral (rutile) is fused with three parts of K_2CO_3, the fused mass powdered and treated with cold water, which removes alkaline silicates, and leaves insoluble potassium titanate K_2TiO_3 together with ferric oxide. This is washed by decantation or on a filter with cold water, and dissolved in cold dilute HCl. On diluting considerably with water and heating to boiling for some time, the whole of the Ti is precipitated as meta-titanium hydrate (Fe being held in solution by the acid), which differs from orthotitanic acid in being quite insoluble in all acids, except concentrated H_2SO_4, while titanium hydrate, obtained by precipitation with alkalies, of exactly the same composition, is readily soluble even in dilute H_2SO_4 or HCl. The precipitated meta-titanic acid is usually tinged yellow, owing to some ferric oxide which is carried down with it. It is best, therefore, to filter off, to wash with a solution of NH_4Cl, and redissolve the precipitate in concentrated H_2SO_4. After dilution with water it is reprecipitated once more by long continued boiling, and this is then all but free from iron. This method answers for the separation of titanium from Al, Be Y and Th.

A more expeditious method for separating the iron oxide consists in precipitating the two metals from the dilute acid solution by means of $(NH_4)_2S$ as FeS and $TiO(OH)_2$, and to treat the precipitate with aqueous sulphurous acid, which dissolves the FeS, and leaves the pure orthotitanic acid.

Another method consists in fusing the titaniferous compound with six times its weight of $KHSO_4$, till it yields a clear mass, dissolve in a large quantity of cold water and acidulate with dilute H_2SO_4, when metatitanic acid is precipitated as above. SiO_2, if present, is not attacked by $KHSO_4$, and remains in the insoluble residue.

The TiO_2 may also be determined by fusion with acid potassium fluoride, and dissolving the fused mass in dilute HCl. The potassium titanium fluoride K_2TiFl_6 formed, which is difficultly soluble in water (1 part requires 96 parts at 14° C.), is collected on a filter, and washed with cold water, and purified by recrystallization from boiling water. Its aqueous solution, when treated with NH_4OH, yields titanium hydrate, which on ignition is converted with incandescence into pure titanium anhydride—white, when only feebly ignited, and yellowish or brownish when intensely heated.

Silica or silicates, containing traces of titanium may be decomposed with HFl. Sulphuric acid should also be added in order to prevent a portion of the titanium from being volatilized with the SiFl formed.

CHAPTER XXVII.

LITHIUM.

HISTORY.—Lithium is the metal of the alkaline base "lithion," discovered by Arfvedson in 1817 in petalite, and found subsequently in several other minerals. The element received its name from the Greek term, meaning stony, because Arfvedson and Berzelius believed that it belonged exclusively to the mineral kingdom. They also imagined that lithium was not absorbed by plants, and sought for it in vain in the ashes of the latter. Subsequently it was shown, however, that lithium occurs in most plants, especially in the leaves, and that the ash of tobacco carries frequently 0.44 per cent. of lithium chloride. The presence of lithium in excess appears to be injurious, however, to plants.

CHEMISTRY AND COMMERCIAL POINTS.—Lithium of atomic weight 7.03 and the specific gravity 0.59 is the lightest of all metals, and floats on naphtha. It is a silver-white body, which oxidizes less rapidly than potassium or sodium, and is softer than lead, but less tenacious. The metal melts at 180° C., and burns with an intense white light, when heated above that temperature. At a degree of heat near 200° C. it attacks silica, glass and porcelain, and volatilizes at a bright red heat in a current of hydrogen. It dissolves rapidly in nitric acid, often with fusion and ignition, and quickly in dilute sulphuric or hydrochloric acids, but slowly in concentrated sulphuric acid.

In order to produce the pure metal, lithium chloride is first fused, and decomposed by the current from a battery of four to six Grove's cells, using a small positive pole of gas carbon and a negative pole of iron wire. In two or three minutes the wire may be withdrawn, and the regulus of lithium of the size of a small pea removed by a spatula beneath rock oil. In this manner an ounce of the metal may soon be reduced. It cannot be obtained by ignition of the carbonate with carbon like potassium and sodium.

Lithium salts are employed to a considerable extent for medicinal purposes, since lithium forms a very soluble uranate. Furthermore the carbonate and citrate are administered to remove uric acid from the blood in gouty affections, or to dissolve calcareous secretions from the human body.

In order to extract lithium salts from lepidolite or petalite, ten parts of the minerals are mixed with ten parts barium carbonate, five parts barium sulphate, and three parts potassium sulphate, and the mixture ignited at the highest temperature of a wind furnace. Two layers are thus produced, the lower of barium silicate and sulphate, the upper of white sulphate of potassium and lithium. It is lixiviated with water and treated with barium chloride to convert the alkalies into chlorides, and precipitate the sulphuric acid as barium sulphate. The solution is evaporated to dryness, and digested with a mixture of equal parts of absolute alcohol and ether, in which the lithium chloride dissolves with only a trace of potassium and sodium chloride.

When using triphylene, it is dissolved in hydrochloric acid, the iron oxidized to ferric chloride by the addition of nitric acid, the phosphoric acid precipitated by the ferric salt formed, the mixture evaporated to dryness, and the remaining mass extracted with water. Manganous and lithium chlorides are thus dissolved; the former is precipitated with barium sulphide, the excess of barium being removed by the addition of ammonium carbonate or sulphuric acid. The solution is evaporated with oxalic acid, and the residual oxalate ignited to carbonate.

Or the finely ground and sifted lepidolite is made into a thin paste with concentrated sulphuric acid in a warmed brick trough, and digested and stirred until it commences to agglomerate. It is then calcined in a reverberatory furnace, and, while warm, well lixiviated with water and filtered. The lye is mixed with sufficient potassium sulphate to convert all the alumina into alum, and the solution decanted from the alum meal. The remaining alumina is precipitated by milk of lime, the alkalies are converted into chlorides by addition of barium chloride, and the solution evaporated to dryness. The chlorides of lithium and calcium are extracted with absolute alcohol, the alcohol is distilled off, and the calcium precipitated by ammonium oxalate, and any heavy metals present removed by adding a little ammonium sulphide. Finally the solution is evaporated in a silver basin.

In case it is intended to extract lithium, caesium and rubidium from lepidolite or petalite, the mineral is fused at a red heat, the fusion poured into cold water, the mass resulting pulverized and washed, and the residue treated with twice its weight of hydrochloric acid. Boil the mass for two hours, filter off the greater part of the silica, add nitric acid to change the ferrous salt dissolved to the ferric state, and precipitate with sodium carbonate, the solution being diluted to such an extent that the lithium carbonate will not be thrown down. After evaporation in an iron vessel, to separate more magnesium carbonate, saturate with hydrochloric acid, and add the proper quantity of platinic chloride to precipitate all the rubidium and caesium. The filtered liquid, containing an excess of platinum and lithium, is treated with hydrogen sulphide to separate the platinum, then concentrated, and mixed with sodium carbonate to precipitate the lithium as carbonate. By this method 1,000 parts of lepidolite will give 78 parts of lithium carbonate, and 6.5 parts of rubidium and caesium chlorides, supposing the operation to be continuous. If thallium is present, which is frequently the case, it will be precipitated as thallium platinic chloride along with the rubidium and caesium.

MINERALOGY.—The rare alkalies, lithium, caesium and rubidium occur only in small quantities in nature, but are widely disseminated. All of them are found in certain mineral springs and plant ashes, those of tobacco and the beet containing appreciable amounts of lithium. Among the minerals carrying these elements, lepidolite or lithia mica, spodumene, a lithium aluminum silicate, petalite of the same character, triphylite, a phosphate of lithium, associated with iron and manganese, and pollucite, a caesium aluminum sodium silicate, are the most important. The first named mineral, lepidolite, is found in aggregates of short prisms, often with rounded terminal faces, also in cleavable plates, but commonly massive, scaly-granular, coarse or fine. Its cleavage is basal and highly eminent. Its hardness 2.5 to 4, its specific gravity 2.8 to 2.9, and its color varies from rose-red to violet-gray or lilac, yellowish, grayish-white and white. Lepidolite is translucent, and has a pearly lustre.

It occurs especially in granite veins, and is often associated with muscovite, as in the rose mica of Goshen, Massachusetts. Other places of occurrence in the United States are Hebron, Auburn, Norway, Paris and Rumford in Maine; Chesterfield, Massachusetts; Middletown, Connecticut, and San Diego, California.

In the closed tube lepidolite gives water, and reaction for fluorine, while it fuses before the blowpipe to a white or grayish mass. It colors the flame carmine at the moment of fusion—a characteristic reaction for lithium. Some varieties give reactions for iron and manganese with fluxes. The mineral is attacked by acids, but not completely decomposed by them. After fusion it gelatinizes with hydrochloric acid. Its composition is as follows:

	I.	II.	III.	
SiO_2	49.62	51.11	49.52	per cent.
Al_2O_3	27.30	25.26	28.80	per cent.
Fe_2O_3	0.31	0.20	0.40	per cent.
FeO	0.07	0.07	0.24	per cent.
MnO	0.55	0.17	0.07	per cent.
K_2O	8.03	10.51	8.82	per cent.
Li_2O	4.34	4.98	3.87	per cent.
Na_2O	2.17	1.43	0.13	per cent.
H_2O	1.52	0.94	1.72	per cent.
Fl	5.45	6.57	5.18	per cent.
CaO MgO	None	0.13	0.15	per cent.
Rb_2O	2.44	1.29	3.73	per cent.
Cs_2O	0.72	0.45	0.08	per cent.
	102.52	103.11	102.74	

Spodumene is another lithium carrying mineral of importance, its average composition, when pure, being given by the figures—

SiO_2	64.2	per cent.
Al_2O_3	27.4	per cent.
Li_2O	8.4	per cent.
	100.0	

It generally contains a little sodium, and the variety "hiddenite," also chromium in cases, to which the emerald-green to yellow color of the mineral is due. The latter is used as a gem, and resembles the emerald. Spodumene occurs mostly in prismatic crystals, which are often flattened and striated, and sometimes very large, but it is found also in massive form. The cleavage of the mineral is perfect, its fracture uneven to subconchoidal, its hardness 6.5 to 7, and its specific gravity 3.13 to 3.20. Its lustre is vitreous, its color varies from greenish-white to grayish-white, yellowish-green, emerald-green, yellow and amethystine purple, and its streak is white. The mineral is brittle and transparent to translucent.

Before the blowpipe spodumene becomes white and opaque, swells up, imparts a carmine color to the flame, indicating the presence of lithium, and fuses to a clear or white glass. The powdered mineral, when fused with a mixture of acid potassium sulphate and fluorite on a platinum wire, gives a more intense lithium reaction. Spodumene is not acted upon by acids.

The mineral occurs at Goshen, Chesterfield, Chester, Huntington and Sterling, Massachusetts; at Windham, Maine; at Winchester, New Hampshire; Brookfield and Branchville, Connecticut; near Stony Point, Alexander county, North Carolina; near Ballground, Cherokee county, Georgia, and at the Etta tin mine in Pennington county, South Dakota, in immense crystals.

The composition of spodumene and hiddenite is represented by the following data:

	Spodumene from Huntington, Mass.	Hiddenite from Alexander Co., N. C.
SiO_2	63.79	64.35 per cent.
Al_2O_3	27.03	28.10 per cent.
Fe_2O_3	0.39	0.25 per cent.
CaO	0.73	None
MgO	0.21	None
Li_2O	7.04	7.05 per cent
K_2O	0.12	None
Na_2O	1.10	0.50 per cent.
Ignition	None	0.15 per cent.
	101.41	100.40

Petalite, another lithium mineral, occurs usually in massive condition, sometimes in tabular form, but rarely in crystals. The cleavage of the latter is perfect, and the fracture imperfectly conchoidal. The mineral has a hardness of 6 to 6.5, a specific gravity of 2.39 to 2.46, a vitreous lustre, is colorless, white or gray, and occasionally reddish or greenish-white. It is brittle, transparent, to translucent, and has an uncolored streak.

Petalite is found in the United States at Bolton, Massachusetts; at Peru, Maine, and at York, near Toronto, Canada. If gently heated before the blowpipe, it emits a blue phosphorescent light, becomes glassy on charcoal, subtransparent and white, and melts only on the edges. It gives the reaction for lithium.

forms a colorless, clear glass with borax, and is not affected by acids. Its composition is shown in the following:

	From Peru, Maine.	
SiO_2	77.29	77.92 per cent.
Al_2O_3	16.95	16.24 per cent.
Li_2O	2.62	3.63 per cent.
Na_2O	2.39	0.51 per cent.
K_2O	Trace	Trace
Ignition	1.03	0.65 per cent.
Fe_2O_3	Trace	0.56 per cent.
MnO	Trace	None
MgO	None	0.24 per cent.
	100.28	99.75

Triphylite, which is next to be considered, is a phosphate of iron, manganese and lithium, corresponding to the formula $Li(FeMn)PO_4$, and verging in color from the bluish-gray triphylite with little manganese to the salmon-pink or clove-brown lithiophilite with but little iron. It occurs usually in massive form and rarely in coarse crystals.

The cleavage of the mineral is perfect, its fracture uneven to subconchoidal, hardness 4.5 to 5, specific gravity 3.42 to 3.56, and its lustre vitreous to resinous. It is transparent to translucent in appearance, of greenish-gray to bluish color in triphylite, also salmon colored, honey-yellow, yellowish-brown, light clove-brown, in lithiophilite; often nearly black on the surface. Its streak is uncolored to grayish-white.

Triphylite decrepitates usually in a closed tube, turns to a dark color, and gives off traces of water. It fuses before the blowpipe, coloring the flame beautifully crimson in streaks, with a pale bluish-green on the exterior of the cone of flame. The coloration of the flame is best seen when the pulverized mineral, moistened with sulphuric acid, is treated on a loop of platinum wire. With the fluxes it reacts for iron and manganese, the iron reaction being feeble in pure lithiophilite. It is soluble in hydrochloric acid.

Triphylite occurs at Branchville, Fairfield county, Connecticut, in a vein of albitic granite in irregular masses, intimately associated with spodumene, and occasionally in rough crystals. It is found also at Tubb's farm, Norway, Maine, and at Norwich, Massachusetts, and with spodumene at Peru, Maine, and at Grafton, New Hampshire.

	Triphylite from Grafton, Light blue.	Lithiophilite from Branchville, Clove-brown.
P_2O_5	43.18	45.22 per cent.
FeO	36.21	13.01 per cent.
MnO	8.96	32.02 per cent.
CaO	0.10	None
MgO	0.83	None
Li_2O	8.15	9.26 per cent.
Na_2O	0.26	0.29 per cent.
H_2O	0.87	0.17 per cent.
Gangue	0.83	0.29 per cent.
	99.39	100.26

Specific gravity of triphylite, 3.549.
Specific gravity of lithiophilite, 3.482.

Finally pollucite, though very rare, and occurring on the island Elba, and at Hebron, Maine, deserves mention. It was found in the latter locality in a single cavity, about a pound in all, in a loose heap, mixed with clay and associated with quartz. The American mineral contained a large amount of caesium, besides small quantities of lithium, as will be seen from the analysis given below. Pollucite occurs crystallized in cubes, and striated transversely, rarely in other forms, and also massive. It has a partial cleavage, conchoidal fracture, is brittle, and has a hardness 6.5 with a specific gravity of 2.901. Its lustre is vitreous and bright on surface of fracture, but sometimes dull and gum-like externally. It is colorless and transparent. The mineral occurs very sparingly in the island of Elba, with petalite, in cavities in granite.

In the closed tube pollucite becomes opaque, and yields water, but only at a high temperature. It whitens in the flame, fuses with difficulty, and colors the flame yellow. Hydrochloric acid decomposes it slowly, pulverulent silica separating out. It analyzes as follows:

	Pollucite from Hebron, Me.	Pollucite from Elba.
SiO_2	43.48	44.03 per cent.
Fe_2O_3	None	0.68 per cent.
Al_2O_3	16.41	15.97 per cent.
CaO	0.21	0.68 per cent.
Cs_2O	36.77	34.07 per cent.
K_2O	0.47	Trace
Na_2O	1.72	3.88 per cent.
Li_2O	0.03	Trace
H_2O	1.53	2.40 per cent.
	100.62	101.71

Specific gravity of mineral from Elba, 2.901.

DETECTION.—Lithium compounds produce a fine carmine red color in the blowpipe flame. They are usually colorless, and when in strong solution, give a precipitate on addition of carbonates or sodium phosphate, in presence of ammonia.

QUALITATIVE DETERMINATION.—By means of the spectroscope the presence of very minute traces of lithium may be readily detected by a brilliant crimson band, lying between the lines B and C, and sometimes a faint yellow line, if the flame of a good Bunsen burner be employed.

$PtCl_4$ produces no precipitate.

Na_2HPO_4 produces on boiling a white precipitate of lithium phosphate $2Li_3PO_4 + H_2O$, very slightly soluble in cold water (2,500 parts), soluble in HCl, and reprecipitated only on boiling, after neutralization with ammonia. Lithium carbonate, especially after having been fused, is difficultly soluble in cold water, hence alkaline carbonates yield from concentrated solutions of lithium salts a crystalline precipitate of lithium carbonate Li_2CO_3 (1 part of the carbonate requires 100 parts of cold water for its solution, but less of boiling water). It is insoluble in alcohol. Hydrated lithium carbonate is soluble in water, and lithium silico-fluoride is almost insoluble in water.

QUANTITATIVE ESTIMATION.—The solution containing the alkalies as chlorides is treated with sodium phosphate, which should be absolutely free from alkaline-earth phosphates, and enough sodium hydrate is added to keep the solution alkaline, when the mixture is evaporated to dryness. Sufficient water is added to dissolve the soluble salts, the solution heated gently, and filtered after twelve hours. The precipitate is washed with a mixture of one part of water and one part ammonia, of which liquid 3.920 parts dissolve only one part of lithium phosphate. The filtrate and the first two washings are evaporated and taken up as before, any residue of lithium phosphate being added to the bulk of the precipitate. The precipitate, dried at 100° C., has the composition of Li_3PO_4.

CHAPTER XXVIII.

CAESIUM.

HISTORY.—This alkali metal was discovered by Bunsen and Kirchoff in 1860, while examining spectroscopically the saline residue obtained by the evaporation of the Duerkheim mineral water. Caesium is the first element discovered by spectrum analysis, and is the most strongly basic and electropositive substance known. It was named from the Latin term "caesius," meaning bluish-gray, on account of the two characteristic blue lines in its spectrum.

CHEMISTRY AND COMMERCIAL POINTS.—Caesium of the atomic weight 132.7, specific gravity 1.38 at 15° C., and melting point 26° to 27° C., resembles potassium in appearance, being silvery-white and soft at ordinary temperatures. It oxidizes quickly, and inflames in air, and decomposes water rapidly with ignition of the liberated hydrogen. Caesium salts are stable, and have a tendency to form double salts; they are isomorphous with those of potassium and rubidium. The metal may be prepared by the electrolysis of a fused mixture of 4 parts caesium cyanide and 1 part barium cyanide, using electrodes of aluminum.

The mineralogical points were given under the caption lithium, the mineral pollucite containing large percentages of caesium.

DETECTION.—Spectrum analysis is to be used in order to discover this element, when two distinct blue lines will be seen in the spectrum. These lines lie near the strontium line, and are seen together with various other less distinctly visible lines in the orange, yellow, and green. When heated on platinum wire in the inner flame of the blowpipe, volatile caesium salts impart an intense sky-blue color to the outer flame.

QUALITATIVE DETERMINATION.—$PtCl_4$ produces a light yellow, crystalline, octahedral precipitate of the double chloride of caesium and platinum chlorides of the formula $PtCl_4.2CsCl$, very difficultly soluble in boiling water—0.377 parts in 100 parts of water. The corresponding potassium platinic chloride is dissolved by repeated treatment with boiling water.

Tartaric acid produces a colorless, transparent, crystalline precipitate of hydrated caesium tartrate, about eight times more soluble in water than the corresponding rubidium salt.

The hydrate $Cs(OH)$ is very soluble, both in water and alcohol, and is very strongly alkaline.

The carbonate $CsCO_3$ resembles potassium and rubidium carbonate, but is soluble in 5 parts of boiling alcohol. (Distinction from K_2CO_3, Na_2CO_3, and Rb_2CO_3, which are practically insoluble in alcohol.) $SnCl_2$, added to a solution of the chlorides of Na, K, Li, Rb and Cs, containing free HCl, forms a heavy white precipitate consisting of nearly pure caesium stannic chloride, $CsCl\ SnCl_4$. By recrystallization from a hot hydrochloric acid solution the crystals are obtained in a pure condition. This reaction affords an easy method of detecting and separating caesium in a mixture of the alkaline chlorides, the chlorides of K, Na, Li and Rb not being precipitated by $SnCl_2$. A hydrochloric acid solution of $SbCl_3$ acts similarly by precipitating a crystalline double chloride $CsCl\ SbCl_3$. The precipitate is decomposed by water, but can be washed, without decomposing, with concentrated hydrochloric acid.

QUANTITATIVE ESTIMATION.—In order to separate the chlorides of caesium and rubidium, obtained by the method given under lithium, the chlorides are converted into carbonates, and to the latter salts a little more tartaric acid is added than is necessary to produce neutral caesium tartrate and rubidium bitartrate. The mixture, having been dried and pulverized, is brought upon a funnel, whose neck is stopped by a small filter, and the whole is placed in an atmosphere saturated with moisture. The neutral caesium salt deliquesces, and passes the filter, while the acid rubidium salt remains behind.

CHAPTER XXIX.

RUBIDIUM.

HISTORY.—This element was also discovered by Bunsen and Kirchoff in the Duerkheim mineral water, immediately after the discovery of caesium. It was called rubidium from the Latin adjective "rubidus," meaning red, for the reason that the spectrum of the element is marked by two dark-red and two violet lines.

CHEMISTRY AND COMMERCIAL POINTS. — Metallic rubidium is a silver-white, soft metal with a yellow tinge, of atomic weight 85.4, and melting point 38.5° C., which evolves a bluish-green vapor at a dull red heat. It oxidizes rapidly in air, and decomposes water with ignition of the hydrogen generated. As to its electropositive properties it is second only to caesium. Its salts correspond with those of potassium, but impart a more reddish shade to the flame than the salts of that metal. Metallic rubidium may be prepared by heating a mixture of sugar charcoal, charred acid rubidium tartrate, and calcium carbonate at a white heat. Commercially the metal or its compounds have found no application unto the present.

As to the mineralogical points rubidium minerals have been mentioned under "lithium"—lepidolite and petalite being especially noteworthy in that regard.

DETECTION.—Also in this case spectrum analysis will be found to be the best means for ascertaining the presence of the element. When thus examined, two dark red lines on the extreme left of the solar spectrum, and close to the potassium line, together with two distinct violet lines, and several weaker lines in the yellow, readily distinguish rubidium compounds. Volatile rubidium salts, when heated on a platinum wire in the inner blowpipe flame, color the outer flame dark-red.

QUALITATIVE DETERMINATION.—The oxide of rubidium, known as rubidia, of the formula Rb_2O, is a powerful base, and its salts are isomorphous with those of potassium. The hydrate $Rb(OH)$ is strongly alkaline, and very soluble in water and alcohol. The carbonate, Rb_2CO_3, is a deliquescent salt, insoluble in alcohol.

$PtCl_4$ produces a light yellow, crystalline precipitate of rubidium platinic chloride, $PtCl_4$ 2RbCl, very difficultly soluble in boiling water. The solubility of the double chlorides of Pt and K, Rb or Cs is respectively as 5.18, 0.634, and 0.377 in 100 parts of boiling water. (Method of separation of K from Rb and Cs.)

Tartaric acid yields a white precipitate of hydrated rubidium tartrate, which is soluble in 10.3 parts of water at 25° C.

Rubidium and caesium resemble potassium also in forming alums, which differ considerably in their solubility in water, 100 parts of water at 17° C. dissolving

13.5 parts of potassium alum, 2.27 of rubidium alum, and only 0.62 parts of caesium alum.

Quantitative Estimation.—The several platinum salts are first prepared, and after having been gently heated in a current of hydrogen, the caesium and rubidium chlorides can be separated from the metallic platinum by hot water. The two chlorides are next converted into carbonates by digestion with silver carbonate. The solution is then evaporated to dryness, and the Cs_2CO_3 extracted with boiling alcohol, Rb_2CO_3 being insoluble in the latter.

Or the carbonates may be converted into acid tartrates by adding to the solution twice as much tartaric acid as is necessary to neutralize it. The two tartrates are separated by fractional crystallization, hydrated rubidium tartrate crystallizing out first, being about eight times more insoluble in water than the hydrated caesium tartrate. On ignition, the pure tartrate yields again the carbonate, from which the various salts are prepared.

APPENDIX.

Analysis of Vanadium and Uranium Ores.

Pulverize the ore to 80-mesh or finer; dry it at a temperature of 100° C. From the dried ore weigh out one gram into a small beaker, and pour over it 25 c.c. of dilute nitric acid (one part of strong acid to three parts of water); digest the ore in the acid on a hot plate for a few minutes, let the insoluble matter settle, and filter off the liquid. Wash the residue with hot water, let the liquid cool, and pass sulphuretted hydrogen gas into it to remove copper, etc. Filter off the precipitate produced by the H_2S, wash it, boil the filtrate and washings to expel the excess of gas, and then add one or two cubic centimeters of hydrogen peroxide to oxidize the iron and vanadium to the highest state; boil to decompose the excess of H_2O_2; let the liquid cool a little, and then add an excess of ammonia and ammonium carbonate, whereby the iron, etc., is precipitated, but the V and U held in solution. The iron precipitate will, however, hold some U and V, especially the latter. Digest the liquid containing the iron precipitate in a warm place for some time, say ten minutes, but do not boil it long enough to decompose the ammonium carbonate.

When the iron precipitate settles, filter it off, and dissolve it in the least possible quantity of dilute nitric acid, reserving the filtrate, which contains the greater part of the vanadium and uranium. Reprecipitate the iron, etc , with an excess of ammonia and ammonium carbonate, digest as before and filter, allowing the liquid to run into the filtrate from the first precipitation of the iron; wash the iron precipitate with hot water, dissolve it in dilute nitric acid, and test the liquid with a drop of H_2O_2. If the solution turns deep red, it still contains some vanadium, and the precipitation with ammonia must be repeated, letting the filtrate run into the beaker containing the filtrates from the first and second separations of the iron. The united filtrates contain all the uranium and vanadium.

The diluted liquid may now be neutralized with nitric acid, and the hydrated uranium oxide thrown down with ammonia, when the precipitate is allowed to settle. The latter is filtered off, washed with dilute ammonia water, dried, and incinerated in an open platinum or porcelain crucible, and weighed as U_3O_8.

Lumps of ammonium chloride are then placed into the filtrate, to eliminate the metavanadate, which separates out within about twelve hours. It is then removed from the mother liquid by filtration, washed with a concentrated solution of ammonium chloride, dried, incinerated in an open crucible and weighed as V_2O_5.

If, however, the titration process is preferred, boil the liquid, which should be contained in a rather large beaker, rapidly to decompose the ammonium carbonate, and expel it together with the excess of ammonia. When this has been effected, the liquid will become cloudy from the precipitation of the vanadium and uranium. After expelling the excess of ammonia, etc., add to the boiling liquid nitric acid, drop by drop, until it again becomes clear, and the precipitate is perfectly dissolved. Remove the beaker from the source of heat, and add to the hot liquid 10 c.c. of a saturated solution of lead acetate. If the excess of nitric acid is not great, a precipitate of lead vanadate will form at once. However, it is necessary to add also a few grams of sodium acetate to insure the complete neutralization of the nitric and the absence of any free acid except acetic acid. The lead vanadate is insoluble in dilute acetic acid, but it dissolves readily in nitric acid. The precipitate is digested on a water bath for a short time until it settles well; it is then filtered off and washed with hot water. The liquid contains no vanadium, but the precipitate is likely to contain a little uranium. Therefore, dissolve it in as little dilute nitric acid as possible (it is very easily soluble); dilute the liquid, add two or three c.c. of lead acetate, and then a little sodium acetate as before. The lead vanadate resulting from the second precipitation is free from uranium. The filtrate from it is added to that obtained from the first precipitation. Dissolve the lead vanadate on the filter paper in dilute nitric acid, and collect the filtrate and washings in a beaker, add to the liquid 25 c.c. of sulphuric acid (half strong acid and half water), and filter off the lead sulphate, evaporate the liquid on a hot plate until heavy fumes of sulphuric anhydride are evolved, cool, take up with water, and transfer to a 10-oz. flask; add 10 c.c. of strong sulphurous acid, which reduces the vanadium from V_2O_5 to V_2O_4. The liquid will turn deep blue. Boil it briskly until the excess of sulphurous acid is expelled, and then titrate the hot liquid with standard permanganate of potassium, one cubic centimeter of which should be equal to about 0.005 grams of iron. The iron value of the permanganate

$$\frac{x\ 182.8}{112}=V_2O_5$$

The liquid containing the uranium contains also an excess of lead and sodium acetates. Add to it 10 c.c. of strong sulphuric acid, and filter off the lead sulphate formed, make the filtrate slightly alkaline with NH_4OH, which will precipitate the uranium as the hydrated oxide, boil the liquid, and let the precipitate settle, filter, but do not wash the precipitate; dissolve it in dilute sulphuric acid (1 to 6), add a little more of the latter acid to it, and evaporate to strong fumes of the anhydride, cool, take up with water, transfer to a small flask, add some granulated zinc, and allow the uranium solution to reduce from the uranic to the uranous form. The zinc should, of course, be free from iron, and the evolution of hydrogen allowed to continue for at least a couple of hours to insure complete reduction. Titrate the reduced solution at room temperature with standard permanganate solution. The iron value of the permangate

$$\frac{\times\ 239.4}{112} = \text{Uranium}$$

Uranium x 1.779 equals the green oxide U_3O_8. The solution, from which the uranium is precipitated as the hydrated oxide, should be dilute (700 to 800 c.c.), as excess of acetates in concentrated solutions is prejudicial to the complete precipitation of ammonium uranate. Ammonium sulphide may be substituted for the ammonia as the precipitant with good results.

Separation of Iron From Uranium.

When, as is generally the case, ammonium carbonate is employed for this separation, it is well known, that some of the iron is always dissolved with the uranium. The following is, however, a method for rendering the separation complete.

As uranium oxide in solution in ammonium carbonate is not precipitated by ammonium sulphide, add to the liquid, separated by filtration from the bulk of the iron oxide, a few drops of $(NH_4)_2S$ to eliminate from it, in the state of sulphide, the small quantity of iron which has been dissolved. After filtering again, a solution is obtained containing all the uranium without any trace of iron.

Analysis of Vanadinite.

One to five grams of the finely pulverized mineral is dissolved in nitric acid, and the copper, lead and arsenic, or any other metal of the second group precipitated by H_2S, which at the same time reduces the vanadium pentoxide V_2O_5 to the tetroxide V_2O_4. The blue solution is then filtered, the filtrate evaporated to dryness, and the residue remaining digested with ammonia, when the vanadium tetroxide becomes reoxidized into the pentoxide, and combines with the ammonia to form ammonium vanadate. Take up with water, filter to remove iron and alumina, and add to the filtrate lumps of ammonium chloride, when ammonium metavanadate, NH_4VO_3, which is scarcely soluble in a concentrated solution of ammonium chloride, will be precipitated. Filter, wash first with dilute ammonia water, then with alcohol, dry, incinerate in an open crucible to expel the ammonia, and weigh as V_2O_5. Vanadium pentoxide melts without decomposition to a yellowish-red mass, when heated, if kept away from reducing agents, and the red liquid crystallizes on cooling. The solid mass has a yellowish-red color.

A Rapid Process.

A rapid progress for estimating the tungsten in metallic tungsten or tungsten powders consists of the following operation: Oxidize to WO_3 by roasting at a red heat, drive off SiO_2 by means of HF, fuse with sodium carbonate, precipitate from neutralized solution with $HgNO_3$, and ignite to WO_3. It is advisable to operate on one or two grams of the tungsten.

Estimation of Molybdic Acid.

Add to the boiling solution of the molybdate lead acetate in slight excess. Boil for a few minutes; the precipitate, at first milky, will become granular, and will subside easily, leaving a perfectly clear supernatant liquid. Care must be taken in boiling, as the thick milky fluid is very apt to boil over. A ribbed filter is to be used, and the precipitate to be washed with hot water. The washing proceeds with great ease and thoroughness, and not the slightest milkiness should be apparent in the filtrate. The precipitate is dried at 100° C., separated from the filter, which it does readily, and ignited at low redness in a porcelain crucible, leaving lead molybdate.

Separation of Tungsten and Molybdenum.

Precipitate the molybdenum and tungsten together by means of lead acetate, wash slightly with hot very dilute acetic acid, and ignite. Transfer to a beaker and dissolve in concentrated HCl, using about as many c.c. of acid as centigrams of the lead salts, and heating just short of the boiling point of the acid. In this way very few irritating fumes are evolved, and the acid is not weakened to any considerable extent before complete solution has been effected. To the clear or possibly faintly opalescent solution add two or three times its bulk of boiling water; boil, allow to settle, decant the clear liquid through a small pulp filter, redissolve in about half the quantity of acid previously used, reprecipitate with water, and filter through the same pulp. The molybdenum is determined in the filtrate, either with or without removing the HCl by precipitation as $PbMoO_4$.

If the amount of tungsten is small compared with the molybdenum, the hydrochloric acid solution of the ignited lead salts, to which a few drops of nitric acid have been added, is evaporated, preferably over the water bath, until nearly pasty, when the WO_3 will have almost entirely separated. The mass is then diluted with 100 to 200 c.c. dilute HCl (3 water to 1 acid), the solution boiled, and the WO_3 filtered off. The weak acid precipitates any WO_3 still unseparated by the evaporation, and is yet strong enough to hold the molybdenum in solution.

Whether the evaporation be performed slowly over the water bath, or more rapidly, some of the WO_3 always adheres to the vessel and cannot be cleared off. A good plan for recovering this consists in dissolving it in two or three drops of dilute ammonia. The solution is then absorbed by a piece of ashless paper, which is ignited along with the main portion of the precipitate.

Detection of Ni, Co, Mn and Zn.

Either one of these four metals can be readily distinguished from the others by adding to the acetate solution first ammonium chloride, then excess of ammonia, and finally an excess of potassium ferricyanide, when one of the following reactions will take place:

1. A brown precipitate—Manganese.
2. A deep-red solution—Cobalt.
3. No change in the cold; on boiling a copper-red precipitate—Nickel.
4. No change in either hot or cold liquid. Add potassium ferrocyanide, white precipitate—Zinc.

Detection of Both Cobalt and Nickel.

To the slightly acid solution, containing nickel and cobalt, add an excess of ammonium chloride, then solution of potassium ferricyanide, until the precipitation is complete, and agitate the mixture under the addition of a large excess of ammonia. Filter, and examine the precipitate remaining as to its color, which, if cobalt is present, will have a characteristic blue tint. The nickel is readily detected in the filtrate by addition of ammonium sulphide. The process is nearly quantitative and may be used for commercial purposes.

Test for Cobalt.

Add to the clear solution, obtained by the acetate method, tartaric or citric acid, then an excess of ammonia, and finally a few drops of a potassium ferricyanide solution. In case cobalt is present, the mixture will assume a deep dark-red coloration. Or add to the perfectly neutral acetate solution, which has been evaporated to a very small bulk, a concentrated solution of sodium sulphocyanate, when, on heating, a blue mass, consisting of cobaltic sulphocyanate, is precipitated, which is readily soluble in water and alcohol, but insoluble in carbon disulphide. Very dilute solutions give, when thus treated at ordinary temperatures, a green color, which becomes blue on heating.

Quantitative Separation of Nickel and Cobalt From Zinc and Manganese.

Bring one gram of the finely powdered ore in solution by means of 10 c.c. sulphuric acid, 5 c.c. nitric acid and 3 c.c. hydrochloric acid, and evaporate to dryness on the water bath. Repeat this operation, in case the ore is not entirely decomposed, take up with hydrochloric acid and hot water, filter, wash, dry, ignite and weigh as acid residue (mainly SiO_2).

Conduct hydrogen sulphide through the filtrate until the smell of the gas becomes permanent, thus removing any of the metals of the second group present, let stand for three hours, and filter off the sulphides, wash with water containing hydrogen sulphide, and heat the filtrate under addition of a few drops of nitric acid or a little potassium chlorate to oxidize the sulphur of the hydrogen sulphide yet remaining and to change the ferrous iron present into the ferric state. Cool, neutralize with ammonia under frequent stirring, until the liquid assumes a deep wine-color, then add a few drops of acetic acid, and an excess of sodium acetate in solid condition. Heat to boiling, continue the ebullition for about five minutes, let settle to see whether the supernatant liquid is water-clear, which it should be, heat again to boiling, add a small crystal of sodium sulphate, which prevents the precipitate of ferric iron, alumina, and phosphoric acid from running through the filter, and pass the liquid through a six-inch filter. Wash slightly with boiling hot water (filtrate I), dissolve the precipitate on the filter in dilute hydrochloric acid, and treat the solution with ammonia, acetic acid, and sodium acetate as before, filter (filtrateII), and combine the two filtrates. Evaporate to about 200 c.c. cool, and acidify with a few drops of hydrochloric acid, heat to change the acetates of the metals present into chlorides, cool, neutralize with ammonia, add a few drops of acetic acid and an excess of sodium acetate, and heat to boiling. Pass a rapid current of hydrogen sulphide through the boiling liquid for half an hour, when every trace of cobalt, nickel or zinc is precipitated in the form of sulphide, while the whole of the manganese remains in solution. Filter off the precipitated sulphides of cobalt, nickel and zinc quickly through a ribbed filter, and wash them with cold water saturated with hydrogen sulphide. Drive off the latter by heating the filtrate, neutralize with a few drops of ammonia, add an excess of ammonium chloride, and precipitate the manganese as manganous carbonate by means of a solution of ammonium carbonate. Allow to settle in a warm place, pass the liquid through a double filter, wash with hot water, dry, ignite and calculate as Mn_3O_4.

Dissolve the mixed sulphides on the filter with the least quantity of dilute nitro-hydrochloric acid, add to the solution, thus obtained, an excess of potassium cyanide, and digest at a gentle heat. Let cool, and precipitate the zinc as ZnS by adding a solution of sodium sulphide as long as a precipitate forms. Allow to stand for a couple of hours; filter carefully, so as to bring the zinc sulphide last on the filter, wash with water containing a little sodium sulphide, and preserve the filtrate containing nickel and cobalt. Dissolve the precipitate on the filter in hydrochloric acid, boil, to drive off hydrogen sulphide, filter if necessary, and precipitate the clear solution with sodium carbonate. To accomplish this, heat the sodium carbonate solution first, and then pour in the liquid containing the zinc. Filter, wash with hot water, dry, ignite and calculate as ZnO.

Heat the filtrate, containing cobalt and nickel as double cyanides, filter and add to it a solution of mercuric oxide in mercury cyanide—readily prepared by boiling mercuric oxide in a concentrated solution of mercury cyanide, and filtering—when all the nickel is thrown down in form of a greenish precipitate, which is to be washed with water, dried, ignited and weighed as NiO. The following equations will explain the reactions occurring:

I. $2NiCy_2 + xHgO + H_2O = HgCy_2 + Ni(OH)_2NiCy_2 + x-1HgO$. (Greenish Precipitate.)

II. $Ni(OH)_2NiCy_2 + HgO = 2NiO + HgCy_2 + H_2O$. (Volatile on ignition.)

The cobalt remains in solution as $K_6Co_2Cy_{12}$, analogous in composition to the corresponding ferricyanide $K_6Fe_2Cy_{12}$.

Neutralize the filtrate from the nickel precipitate with dilute nitric acid, and add a neutral solution of mercurous nitrate, $Hg_2(NO_3)_2$, which is best kept in the mercurous state by adding a few globules of metallic mercury to the aqueous liquid. A white precipitate of mercurous cobalticyanide of the formula $(Hg_2)_3Co_2Cy_{12}$ forms, which contains the whole of the cobalt. Filter, wash and ignite under a hood, when cobaltous cobaltic oxide of the composition Co_3O_4 remains.

Quantitative Estimation of Chromium.

Place one gram of the ore in a porcelain dish together with a quantity of nitric acid and some potassium chlorate, and cover the dish with a reversed funnel. Heat, and add fragments of potassium chlorate, from time to time, through the stem of the funnel, until the chromic oxide has completely dissolved, which usually takes place in about half an hour. Filter, dilute with water, neutralize the filtrate with ammonia, and add sufficient acetic acid to make it slightly acid, cool, add a solution of barium chloride in slight excess, and allow to settle for twelve hours.

Wash the precipitated barium chromate by decantation with a cold solution of ammonium acetate, to remove barium salts, that may have been carried down with the chromate, filter, rinse with water, dry, heat in a crucible to expel the last traces of water and ammonium salt, ignite and weigh as $BaCrO_4$.

Or add mercurous nitrate to the boiling solution containing chromic acid, obtained by neutralizing with sodium carbonate, allow the orange-red precipitate of mercuric chromate to stand for some hours, filter, wash with a hot but weak solution of mercurous nitrate, dry, and heat to redness in a crucible, until pure chromium trioxide Cr_2O_3 remains.

Very accurate results may be obtained by precipitating with barium acetate at a boiling heat, adding a small quantity of strong alcohol to the liquid, allowing the precipitated chromate to settle completely, so as to leave the supernatant liquid quite clear, washing with water containing one-twelfth of its volume in alcohol, and filtering, drying and igniting. This method is the shortest, since the filtration and the washing may be executed almost immediately after precipitation.

Volumetric Estimation of Antimony.

The finely pulverized sample, one-half or one gram, is treated in a beaker with 50 c.c. hot water and 50 c.c. strong HCl, the water being added first. Heat on sand bath at 70° C., for one-half to one hour. Filter in large beaker or flask, washing with dilute

HCl and water. Add tartaric acid to filtrate, dilute to about 750 c. c., heat to 70° C., and precipitate with H_2S. Filter, wash with hydrogen sulphide water, then bring the precipitate back into the precipitation vessel with the aid of hot water. Warm the sulphide with 50 c.c. strong HCl, avoiding to heat to boiling, until no more H_2S is evolved. The presence of H_2S is at once detected, if a little cold water be added to the solution, by the reappearance of a precipitate of red Sb_2S_3, the addition in the absence of H_2S causing only a slight milkiness, due to basic chloride. When all H_2S is expelled, the liquid is diluted, the turbidity is removed by just sufficient HCl added drop by drop, and the solution titrated with permanganate.

$$5SbCl_3+16HCl+2KMnO_4=5SbCl_5+2KCl+2MnCl_2+8H_2O.$$

If 5.27 grams of $KMnO_4$ be dissolved per liter of solution, one c.c. will equal 1 per cent. Sb with one gram sample. The endpoint of the reaction is sharply defined.

Volumetric Method for Determining Magnesia.

Pour the solution, which should not contain too great an excess of ammonium chloride or ammonium oxalate into a large Erlenmeyer flask, add one-third the volume of concentrated ammonia and 50 c.c. of standard sodium arsenate. Cork up tightly and shake vigorously for ten minutes. Allow the precipitate to settle somewhat and wash with a mixture of three parts water and one part strong ammonia, until the washings cease to react for arsenic; avoid using an excess of the washing fluid, however. Dissolve the precipitate in dilute hydrochloric acid (1:1), allowing the acid solution to run into the flask in which the precipitation was made, and wash the filter paper with the dilute acid, until the washings and solution measure 75 or 100 c.c. Cool, if not already so, and add from 3 to 5 grams of potassium iodide, free from iodate; allow the solution to stand a few minutes, and then run in standard thiosulphate, until the color of the liberated iodine fades to a pale straw color. Add starch and titrate until the blue color of the iodide of starch is discharged. If preferred, an excess of thiosulphate may be added, then starch and standard iodine, until the blue color is produced. On adding the iodide of potassium to the acid solution, a brown precipitate forms, which, however, dissolves when the thiosulphate is added.

The standard solution of sodium arsenate is prepared by dissolving 12.29 grams of pure arsenious acid in nitric acid, evaporating to dryness on a water bath, neutralizing with sodium carbonate, and diluting to one litre. Each c.c. of this solution is equivalent to 0.005 gram of magnesium oxide.

Separation and Estimation of Potassium and Sodium in Rocks.

The silica is determined as well as the oxides of iron and aluminum; the lime, magnesia and sulphuric acid magnesium; filter, wash, ignite and weigh; the attack with carbonate of lime (1 gram of rock to 0.5 gram of carbonate of lime) is effected in an assayer's furnace, for the estimation of the alkaline metals. The amount of silica is checked. As for the oxides of iron and aluminum, the lime and magnesia, the results here obtained are generally incorrect, no matter what care may be used in the separation of these bodies, on account of the dissemination of the large quantity of lime added. The separation and estimation of the potash and soda are effected in the following manner: The silica, oxide of iron, aluminum and lime are eliminated in the ordinary manner. The remaining solution is evaporated to dryness on the waterbath, and the ammoniacal salts (oxalate, acetate, and chloride,) are driven off by heat. Take up with water, and separate the magnesia in the form of ammonium-magnesium-phosphate; this is the only manner in which it can be entirely got rid of. The ammonia is driven off, and the phosphate of ammonium precipitated by a fresh solution of pure neutral acetate of lead at ten per cent. in large excess. Filter and remove the excess of lead by means of hydrogen sulphide. After filtration and evaporation of the liquid on the waterbath, the residue is heated to dull redness, taken up with very dilute hydrochloric acid, filtered, and concentrated. The potassium is precipitated by platinic chloride with alcoholic ether added. Filter, and wash with alcoholic ether; dissolve the potassium platinic chloride in warm water; displace the platinum by magnesium; filter. wash, ignite and weigh; the platinum precipitated corresponds to the potassium.

From the solution separated from the $PtCl_4.2KCl$, the alcoholic ether is driven off by heating, the platinum is precipitated with H_2S while hot; this is then filtered, the filtrate evaporated, and the residue brought to a red heat after the addition of sulphuric acid. This leaves sulphate of soda, which is weighed, and can then be crystallized.

Estimation of Sulphur in Coal.

Mix intimately one gram of the finely powdered coal with one gram of calcined magnesia, and one-half gram of dried sodium carbonate by means of a glass rod in a platinum crucible, and place the latter in an inclined position on a clay-pipe triangle. Apply a gentle heat with a Bunsen burner, so that only the lower half of the crucible shows a dull red heat, and stir the mixture by means of a heavy platinum wire, every five minutes, for an hour. Let cool completely, and mix intimately one gram of ammonium nitrate with the mass in the crucible, and heat for ten minutes, the crucible being covered with the lid. Pour the mass into a beaker, tapping and gently squeezing the crucible, add water, and warm, and extract the remainder adhering to the crucible by filling the latter repeatedly to half its capacity with water and warming. Filter the combined liquids, heat, and add barium chloride to the filtrate, to precipitate the sulphuric acid formed as barium sulphate. Filter, wash, dry, ignite and weigh as $BaSO_4$.

Electric Furnace.

A new form of electric resistance laboratory furnace has been invented by Professor Holborn of Berlin, which permits of temperatures up to 1,500° C. being attained with ease by use of the ordinary 110-volt electric supply. The furnaces are made in two forms, the first being adapted for heating crucibles, and the second for heating tubes 44 centimeters in length. In both forms of furnace the electric current is conducted through a resistance coil of platinum or nickel wire, wound round a thin porcelain tube or cylinder. The crucible or substance to be heated is placed within this latter, and the space between the outer side of the coil and the containing vessel is packed with asbestos or powdered quartz. Using nickel, the temperature of the furnace cannot be raised above 1,000° C. without damage to the coil, but with platinum it is possible to attain a temperature of 1,500° C. with a current of 14 amperes and 110 volts.

THE CHEMICAL ANALYSIS OF CRUDE PETROLEUM AND OIL ROCK.

The analysis of crude oil begins with the determination of the smell of the liquid—a sweet odor indicating the presence of a paraffine base—a petroleum smell, familiar to everyone, that of a petroleum base—and an asphalt odor, also readily recognized, the presence of an asphalt base. This preliminary test is.

however, to be confirmed by subsequent observations and results obtained during the course of the analysis, and is followed by the determination of the specific gravity and degree, Beaume, of the oil, which is best accomplished by means of a hydrometer for light liquids, having the corresponding degrees of each marked on the scale. In conformity with the course of manufacture chosen by the refineries, the oil is then subjected to the distillation test by weighing off about fifty grams of it, if the sample is large enough, or less, in case the amount of liquid at disposal is but limited. Some chemists refer their analytical data, however, to volume, but it will be readily seen that this method does not cover all cases. Whenever the bulk of the oil, submitted for analysis, is very small (which is frequently the case), the several fractions produced by distillation will be but diminutive, so that the accurate measurement of the latter becomes very difficult, if not impossible. Besides, the reduction of the weights of the fractional distillates to volumes offers no special difficulty, as the absolute weights of these products are well known, and the proportions in bulk can be readily ascertained by simple calculations.

The weight of a small Erlenmeyer flask, which fits the balance better than any other vessel, plus the oil to be distilled having been ascertained, the fluid is poured from the vessel into the bottom of a medium sized glass retort, care being taken not to touch the tubular opening made for the insertion of the glass stopper, nor the inner sides of the retort with drops of the oil. The flask, containing the rest of the liquid, is then weighed, the weight of the oil to be subjected to distillation, ascertained by subtracting the second weight from the first, and a thermometer inserted into the tubular opening of the retort. To effect this insertion a short piece of rubber tubing is pushed over the stem of the thermometer, which assures a tight fit, and the instrument is placed in such manner that its bulb stands within about an inch above the surface of the oil to be distilled, so that, on heating, the temperatures of the oil vapors arising can be readily read from the scale of the thermometer. The bottom of the retort, thus provided with the oil and thermometer, is then placed upon a pipestem triangle, resting on a tripod, without any further protection of wire gauze or other material, and the neck of the retort steadied by means of a support, its mouth being inserted into a receiver, consisting of a small, tared, Erlenmeyer, which rests in a porcelain dish, filled with a freezing mixture of ice and salt and covered with a piece of heavy filtering paper.

In case the oil contains highly volatile hydrocarbons, liable to distil below the boiling point of water, as rhigolene, boiling at 18.3° C. or 64.9° F., petroleum ether, or gasoline, boiling between 70 and 90° C., or 158 and 194° F., the bulb of the retort is placed in the ring of a water bath, so that the surface of the oil reaches below the level of the ring, when the water in the bath is gradually heated to 18.3° C. or 64.9° F.

This temperature is maintained for about fifteen minutes, and the fraction, thus collected, weighed. It is essential to rotate the receiving flask continually during this and the subsequent distilling operations, so as to assure the condensation of the oil vapors as completely as possible; also to close the flask by means of a cork or glass stopper immediately after removing it from the neck of the retort, in order to prevent loss by evaporation, when carrying the flask to the balance, and weighing. If a common cork is used for this purpose it should be dry, smooth and tight-fitting, and be inserted into the mouth of the flask to a certain mark, made with a pencil, and be weighed with the flask while in this position. A glass stopper ground to fit the neck of the flask is, of course, preferable, and a dozen of such flasks, perfectly dry and clean, should be kept ready and numbered and weighed beforehand.

These preparations having been made and the volatile parts of the oil, distilling up to 90° C., been determined, the retort is removed from the water bath, dried and placed upon the pipestem triangle, mentioned before. A very small gas flame is now cautiously applied to the bottom of the retort, the burner being constantly moved from side to side, and the temperature gradually raised to 110° C. or 230° F., another flask having been substituted to receive the naphtha now distilling, which is removed to be weighed and replaced by another flask. In the same manner the ligroine portion, distilling up to 120° C.

or 248° F., may be gathered and weighed, and finally the benzine fraction, distilling between 120 and 150° C., or 240 and 302° F., when the operation of changing the flask and weighing it is repeated. This done, the temperature is raised from 150 to 200° C. or 240 to 392° F., when an exchange of flasks and weighing takes place, then to 250° C. or 482° F., and finally from 250 to 300° C., or 482 to 572° F., followed by the same manipulations as before. The weights of the oils, separated by these three last operations, are added and considered as the amount of illuminating or burning oil (kerosene) present, but are best given separately in the report, while the percentages of the volatile oils, determined before, are frequently obtained together in one distillation, and figure then in the reports under the popular caption of light oils or naphthas. In case the specific gravities and the degrees of Beaume of these fractional distillates, obtained so far, should be required, the original weight of the crude oil employed must necessarily be increased or the distillation repeated several times, for the reason that the volumes of the several fractions collected from about fifty grams of the oil are too small to allow of the determination of these points by means of a glass cylinder and hydrometer.

This stage of the process having been reached, the thermometer is removed from the tubular opening of the retort, and replaced by the glass stopper belonging to it, which is tightly fitted, so that the heating above 300° C. may be safely continued, a new receiving flask having been brought in place. The distillation is then started again, the heat given by the burner increased, and the driving over of the oil continued, until the carbonaceous residue remaining on the end is void of oil and perfectly dry. The distillates thus resulting are weighed in one body, and represent the heavy hydrocarbons or lubricants, containing sometimes paraffines, which are separated from the liquid by immersing the flask containing it in a freezing mixture, when the paraffine will separate out in a semisolid mass. The latter is freed from the lubricants, mixed with it, by bringing it quickly into the perforated bottom of a lemon squeezer, which is provided with an inside layer of calico or similar fabric, folded closely over the upper part of the mass, and applying very carefully a gentle pressure by means of the upper lid, when the lubricants will drip into a tared beaker or other suitable vessel, placed underneath, and small enough to allow of ready handling on the balance. The solid paraffine remaining in the receptacle in form of a spherical cake is then broken into pieces, melted and allowed to crystallize, and again worked in the squeezer, when it is ready to be weighed as "refined wax." In case it should be desired to ascertain the amount of "block paraffine" contained in the wax, it is washed with benzine, pressed again, melted and filtered through bone black, when it will be found to represent a perfectly clear and colorless liquid, which solidifies to a hard, translucent mass on cooling. When performing this operation the employment of a funnel, made from sheet iron, which can be conveniently warmed by the flame of a Bunsen burner, will be found of great service, since it prevents loss of paraffine to a considerable extent.

Instead of extracting the paraffine from the lubricants it can also be obtained directly from the crude oil. For that purpose a portion of the latter is placed in a flask, mixed with three times its volume of ether, the liquid well shaken, and the vessel placed into a freezing mixture, when nearly all the paraffine present will separate out. It is removed from the mass by filtering and treated in the same manner as shown above.

The recovery of the oil from oil sand and shale on a laboratory scale is, according to the experience of the writer, most conveniently accomplished by passing the shale or rock through a crusher and reducing it to the size of small pebbles.

On the other hand, the oil sand may be reduced to this condition, if not hardened too much, by breaking it with a hammer on an iron plate. The weighed mass is then placed by portions into the receptacle of an iron retort, used for distilling the mercury from gold amalgam, when the lid and delivery tube are attached, and the retort is placed into the partition of a gasoline furnace serving for crucible assays. In order to prevent the loss of heat as much as possible, the retort is inserted into a circular opening of its own size, cut from a heavy asbestos sheet, which covers the remaining open space of the partition. A gentle heat is then applied, and the latter gradually raised until yellow vapors appear at the mouth of the delivery tube, which enters a roomy, tared flask, placed in such manner that the tube reaches down to the upper center of the vessel. The flask itself rests in a basin, filled with ice and salt, and is covered with a cloth saturated with ice water, so that all condensible vapors are readily liquefied. Fifty to sixty pounds of oil sand or rock can be worked thus in the course of a day, after which the flask, or flasks, containing the oil are weighed and the weight of oil obtained in this manner is calculated. The product thus resulting is then subjected to fractional distillation, and the composition of the oil ascertained according to the method described before.

The analysis of the oil having been carried out to this point, the determination of the flashing and burning points of the crude oil and of the illuminating and lubricating portions is now in order. The flashing point of kerosene or illuminating oil has been fixed by legislature for the city of Denver at 110° F. or 43.3° C., the test being executed in an open metal cup, which contains the oil to be examined. A thermometer is inserted into the oil in the cup, which rests in a water bath, and the oil is heated indirectly from beneath by an alcohol lamp, while a burning splinter of wood or an electric spark is passed at intervals of two or three degrees of the thermometer scale over the surface of the liquid. On raising gradually the temperature of the oil, which is agitated from time to time by means of a glass rod, so as to produce uniform conditions, it finally reaches the point of "flashing," and at the moment when the flickering occurs the thermometer is read and the flashing point thus ascertained.

A great number of apparatus, whose construction is based upon the principle described, have been introduced, the first contrivance of this kind having been constructed by Tagliabue, an instrument maker of New York. It consists of a glass cup, holding the oil, which is placed in a water bath, made of copper, and heated by means of a spirit lamp. A thermometer is suspended in the oil and the temperature noted at which a lighted chip of wood or match, passed over the heated liquid, induces the production of a flash.

It will be seen that an apparatus answering for the determination of the flashing point can be readily constructed by fitting a small metal cup or beaker, containing the oil to be tested, into the ring of a water bath, immersing a thermometer, supported by a stand, into the liquid, and heating according to the directions given above. Another manner of arranging an apparatus of this kind consists in placing a small beaker containing the oil and suspended in a triangle into a larger one, filled with water and serving as a water bath. The thermometer is then introduced into the oil and the test finished as indicated before.

As to explosions caused by improperly refined petroleum when burned in lamps, it is generally conceded that an oil having a flashing point, lying below

21° C. or 70° F., is to be considered as a dangerous illuminant; but the refining of crude oil has been perfected in recent years to such an extent that accidents of this kind belong to the rarities. Moreover, it is in the interest of the manufacturer to remove the volatile hydrocarbons from the bulk of the oil as completely as possible, since these fluids bring a very high figure that of rhigolene f. i. amounting to seventy-five cents per pint in the retail trade.

To satisfy, however, the most exacting, the kerosene fraction is subjected in most refineries of the United States to a practical burning test in lamps of the usual construction, and the decrease in the size of the flame in a fixed period noted as well as the volume of the oil consumed. To facilitate these observations a special lamp, constructed by Saybolt, has been introduced, consisting of a cylindrical, graduated glass reservoir of small diameter, forming the stem of the lamp, and joined to a heavy glass foot, the whole being surmounted by a graduated glass chimney. The burner of the lamp furnishes a well shaped flat flame of considerable height in proportion to the width, and is provided with a carefully selected wick. While the observations referring to the height of the flame and the corresponding consumption of the oil are made, the lower part of the lamp is placed in a vessel filled with water of 15.5° C. or 60° F., so as to keep the oil at a steady temperature while being burned and tested.

A method similar to the one described above for making the flashing test is employed by United States inspectors for examining lubricants, and recourse is taken for this purpose to the determination of the burning or fire test, that is the degree of heat required to ignite the oil and cause its continued burning. In this case an open metallic cup is used, which rests on a tripod, and is heated directly by the flame of a spirit lamp, the temperature being read as usual, by a thermometer inserted, and the heat raised at the rate of 8° F. per minute; or the volatility of the oil is ascertained by noting the loss in weight, sustained by a given quantity of the oil, when exposed for a specific length of time in a shallow vessel to a high temperature. A good method consists in exposing twenty-five grams of the lubricant for twelve hours in a shallow dish to a temperature of 65.5° C. or 150° F., when testing engine and spindle oils, and to raise this degree of heat to 121° C. or 250° F., when testing cylinder oil.

Naturally occurring lubricating oils, like those of Pennsylvania, Ohio, West Virginia and Kentucky, are classified according to their specific gravity and degree of Beaume, besides being tested according to the following directions, established by the West Virginia Transportation Company:

"In receiving and making delivery of oils shipped by the company, the water and sediment contained therein shall be determined by mixing an average sample with an equal quantity of benzine and subjecting the mixture to 49° C. or 120° F. in a graduated glass vessel for not less than six hours, after which the mixture cools and settles not less than two hours for light grades, three hours for A grade, four hours for B grade, six hours for C grade, eight hours for D grade, and eighteen hours for heavier grades.'' The grades are as follows:

A—37.1° Beaume, about 0.838 specific gravity and lighter.

B—33° to 37° Beaume, and 0.859 to 0.838 specific gravity.

C—31.6° to 32.9° Beaume, and 0.870 to 0.859 specific gravity.

D—30.6° to 31.5° Beaume, and 0.873 to 0.870 specific gravity.

E—29.6° to 30.5° Beaume, and 0.877 to 0.873 specific gravity.

F—28.6° to 29.5° Beaume, and 0.883 to 0.877 specific gravity.

G—28.5° Beaume, and 0.883 specific gravity and heavier.

Furthermore, ordinary crude petroleum, from which kerosene and the other usual commercial products are manufactured, is required by the New York Produce Exchange to be ''pure natural oil,'' neither steamed nor treated, free from water, sediment or any other adulteration, of 43° to 48° Beaume, and a specific gravity lying between 0.809 and 0.786. In order to ascertain whether the petroleum is a ''pure, natural oil,'' a sample is subjected to fractional distillation, each fraction being one-tenth of the crude oil by volume, when the degrees of Beaume and specific gravities of the several distillates are determined. The regular gradation in the degrees of the fractions is considered as a satisfactory indication that the oil is a pure natural product.

The analysis of the oil having been carried out to this point, there remains the establishment of the degrees of viscosity of the fractions, the results obtained by the process employed forming the basis for the grading of the lubricants. A very simple apparatus, serving the purpose in view, may be constructed by selecting two pipettes of equal orifice and capacity, and placing them into the clamps of a burette support. One of these pipettes is to be standardized by filling it to the mark with a standard oil, preferably sperm oil, and fastening it into the clamp, when its vertical position having been assured, the liquid is allowed to run into a vessel placed underneath. The time consumed by the running out of the oil is marked by means of a watch, which is suspended from a nail driven into the top of the staff of the stand, so as to facilitate the taking of the time by the operator. The oil to be tested is now drawn into the second pipette, and the latter placed into the other clamp of the support, when it is adjusted and also allowed to empty its contents, the time required for this operation being read from the watch. The relation of the two data found indicates the degree of viscosity of the sample tested in comparison to that of the standard oil, the principle underlying the test being the well-known fact that specifically light liquids leave the orifice of the pipette in less time than heavy fluids.

This rather primitive viscometer, described above, has, however, been improved to a great extent, and very reliable and accurate apparatus have been constructed in later years, among them the Saybolt, Redwood, Engler, Mason and Lepenau, which differ essentially from one another in construction, and, therefore, require special inspection in order to effect successful manipulations.

Thus the viscometer of Lepenau consists of two similar metallic cylinders, placed vertically side by side in a water bath, and provided with three pairs of interchangeable jets to be inserted in the stopcocks at the bases of the cylinders. A standard oil having been placed in one cylinder, and the oil to be tested in the other, a pair of jets delivering the oil in drops is selected, and the number of drops falling from the two cylinders between two coincidences of dropping is noted.

Similar arrangements can also be made with the pipette apparatus by attaching to the orifices of the instruments two pieces of rubber tubing of equal length, into which two exactly perforated narrow metallic jets have been pushed, and observing the falling of the drops.

It will be seen from the foregoing that the determination of the viscosity of an oil must necessarily be an arbitrary one, no general standard liquid nor uniform width of the jets or pipettes used having been accepted so far, though pure sperm oil is usually employed. On reporting the results obtained in the manner indicated, it is, therefore, proper to give the grade of the standard oil chosen, the name of the firm which furnished it, and the viscosity of the liquid as given by that concern.

RADIUM.

History.—The discoverer of this rare element is Madame Sklodowska Curie, a French lady of Polish descent, and the first of her sex in the history of chemistry to accomplish such a deed. In 1899 she began her researches about the rays emitted by uranium, which had been discovered by Becquerel and named from him Becquerel rays. These investigations led her gradually on to the discovery of radium, and gained so much in interest and importance in the course of time, that they caused her husband to lay down the work in which he was engaged and to join his wife in her aspirations. The product of their united efforts was the discovery of several so-called "radio-active" bodies—a term invented and introduced by the renowned lady herself.

Radium, polonium and actinium were the three new bodies examined. The first of these accompanies the barium precipitate obtained by the chemical treatment of pitchblende or carnotite, the second is analogous to bismuth and separates out on subliming the sulphide in vacuo—the radio-active sulphide being much more volatile than the ordinary bismuth sulphide. Polonium may also be prepared by precipitating a solution of bismuth nitrate by water—the precipitated basic nitrate being much more active than the salt which remains in solution. Finally polonium may be obtained by precipitating a strongly hydrochloric acid solution of bismuth with hydrogen sulphide, when sulphides are obtained, which are considerably more active than the salt remaining dissolved. The third radio-active body discovered was found to be an associate of the iron group accompanying pitchblende, and seems to be allied in particular to thorium, from which it has not yet been found possible to separate it.

Of these three radio-active bodies, which all occur in pitchblende in quite infinitesimal amounts, polonium was discovered by M. and Mme. Curie alone, radium also by them in conjunction with the scientist, Bemont, and actinium was identified by the chemist, Debierne, who also named it.

Chemistry and Commercial Points.—The atomic weight of radium has been found to be 225 by Mme. Curie, who prepared and used the pure radium chloride for this determination. The metal radium has not as yet been prepared.

In order to obtain radium from carnotite, the pulverized ore is dissolved in hydrochloric acid, a little nitric acid being added. Most of the acid is then evaporated, the residue mixed with water, and the liquid part filtered off. Dilute sulphuric acid is now given to the solution in small quantity to precipitate the barium, and the mixture allowed to stand for several hours, when it is filtered.

It is the precipitated sulphate of barium, which contains the diminutive radium values, and the latter are obtained from the precipitate by repeated fractionations. It is estimated that a ton of carnotite contains about five grains of radium, and as the chemistry of that element is almost unknown, a considerable waste of the valuable material takes place at every step of the operation. Very many tons of carnotite would have to be treated, therefore, to produce an appreciable quantity of radium, and that result could only be reached in a very well-equipped laboratory under the assistance of highly skilled assistants. The German manufacturer, who is selling radium bromide at the price of $2.25 a milligramme, is only able to supply it, because he was fortunate enough to get hold of some very rich residues, which had been accumulating for many years at the uranium works at Joachimsthal, Bohemia. Such being the case, it would be preferable to buy the radium from Germany rather than spend six months' time and a large amount of money in preparing it.

Furthermore, in addition to the work involved, it would not be worth while to embark in that enterprise, unless the manufacturer could treat ten or fifteen tons of the raw material per day, and, at the same time, have a well-appointed laboratory and experienced chemists to perform the subsequent operations. The price of radium bromide at $2.25 a milligramme will be maintained so long as only a limited number of milligrams is in existence. It would be out of the question, however, to reckon on selling radium by the ounce or the pound at such a figure. Hence, if anyone, entering in the manufacture of radium from carnotite, should expect to realize that figure or even a tenth of it by the pound, he would be disappointed. At a much lower price the demand for radium would be good, but it is doubtful whether this demand would ever be much greater than it now is at the present figure.

MINERALOGY.—With reference to the mineralogy of radium it can only be stated that the element is present in the uranium ores, pitchblende and carnotite. Protracted research will, however, it is hoped, allow a better insight into the mineralogical points of the element.

DETECTION.—The new element can be detected by spectrum analysis—a method which served Mme. Curie as a means of bringing conviction to herself, when still in doubt as to the interpretation of the result of her researches. The radium line is found in the ultra violet, and the general aspect of the spectrum is that of the metals of the alkaline earths. These metals are known to have well-marked line spectra with certain nebulous bands. Qualitative or quantitative determinations of radium are naturally out of the question on account of its scarcity and the present condition of our knowledge of this remarkable body. Instead of directions in that regard we can give, however, the following information about its peculiarities and the characteristics of the radium salts:

From its chemical properties, radium is an element of the group of alkaline earths, being the member next above barium. From its atomic weight also, radium takes its place in the periodic system of the elements after barium with the alkaline earth metals, in the row which already contains uranium and thorium.

The salts of radium, as the chloride, nitrate, carbonate and sulphate, resemble those of barium, when freshly prepared, but they gradually become colored. All the radium salts are luminous in the dark. In their chemical properties, the salts of radium are absolutely analogous to the corresponding salts of barium. However, radium chloride is less soluble than barium chloride. The solubility of the nitrates in water is approximately the same. The salts of radium are the source of a spontaneous and continuous evolution of heat. Radium is a bivalent element, the chloride having the formula $Ra\ Cl_2$.

N. B.—The address of the radium merchant (!) is Herr H. Buchler, Chinin Fabrik, Braunschweig, Germany. The price he charges is $2.25 a milligramme for nearly pure radium bromide—as stated before—or $3.00 a milligramme, if highly purified. This works out at $3,000 a gramme.

MOLYBDENITE AND THE COMMERCIAL PRODUCTS DERIVED THEREFROM.

Molybdenite is a mineral which has come lately to the front, the main reason for this condition being its applicability, in the form of metal or ferro-molybdenum, to carbon steel, whereby the properties of the latter are essentially improved. It is even claimed that the molybdenum steel, obtained in that manner, is superior to any kind of steel known, tungsten steel not excepted. Consequently the demand for molybdenite has considerably increased, and since it is more generally known, that the mineral occurs in Colorado and Oregon in commercial quantities, eastern firms have made the most tempting offers to producers of molybdenite by stating their desire of buying large quantities per month by contract or of handling the whole output of the mine at good figures, even before the working of the deposit was started.

These favorable commercial conditions are furthermore explained by the fact that buyers of molybdenite were formerly obliged to import their merchandise through the assistance of foreign agents from middle Europe, and at a figure, which was almost prohibitive to making reasonable profits. It is to be expected, therefore, that the course of the trade in molybdenite will be materially changed, and that the states of Colorado and Oregon will be able to fill with facility any demand for that mineral in the near future.

It is to be known, however, that molybdenite itself, which is a sulphide of molybdenum of the formula

MoS_2 and consists of 60 per cent. metallic molybdenum and 40 per cent. sulphur, can not be applied as such for the improvement of steel, and must undergo a treatment by which every trace of sulphur is removed. This operation is effected either by roasting the ore or by treating it with nitric acid, when, in either case, the trioxide, MoO_3 results, which may be reduced, under the addition of carbon in the electric furnace to molybdenum carbide. The carbide, thus obtained, is then fused with iron in the proportion desired to produce ferro-molybdenum, and the latter alloy is added, enclosed in an iron tube, to the molten steel. This complicated proceeding is necessary for the reason that the presence of the smallest percentage of sulphur in steel destroys its good properties and renders it brittle, or cold-short, so that it breaks when bent.

In case the roasting of the ore is resorted to, it is desirable to effect as dead a roast as possible, so as to change most of the molybdenum present into the trioxide and the sulphur into the dioxide, which escapes, thus:

$$MoS_2+7O=MoO_3+2SO_2.$$

The process is rather favored by pulverizing the mineral finely, stirring from time to time, and applying a gradually increasing heat, which may be brought to the highest temperature obtainable in the muffle or wind furnace, since molybdenite has not been known to fuse under these conditions. Whether the heat of the electric furnace is sufficient to produce that result is not known, but it is to be assumed that decomposition will take place before melting, and that the two elements, molybdenum and sulphur, will be volatilized. The molybdenum trioxide, obtained in the manner described above, is then extracted from the roasted and cooled mass—which contains also the foreign admixtures of the ore—by the addition of ammonia, in which the trioxide dissolves, forming ammonium molybdate, as shown by the following equation:

$$7MoO_3+14NH_4OH=7(NH_4)_2MoO_4+7H_2O,$$

which may be represented in a more simple manner as

$$MoO_3+2NH_4OH=(NH_4)_2MoO_4+H_2O,$$

but had to be given in the first form on account of the fact that the molybdate thus obtained changes on evaporation into a complex salt, containing seven atoms of molybdenum, as will become apparent from the equation presented here:

$$7(NH_4)_2MoO_4 \text{ if evaporated, becomes}$$
$$[(NH_4)_6Mo_7O_{24}+4H_2O]+8NH_3.$$

This salt crystallizes finally from the ammoniacal solution, and is a commercial product, which finds extensive application in chemistry for the detection and determination of phosphorus and the estimation of lead by titration.

On adding ammonia to the roasted molybdenite the majority of the metallic oxides present as impurities remain undissolved, sulphur besides arsenic and antimony, eventually contained in the mineral, having been volatilized by the heat, but copper, which has been changed into the oxide by the roasting process, dissolves in the ammonia to a blue solution, and should be removed. As the elimination of this metal is a troublesome affair, and especially when working voluminous quantities of solution, buyers demand a mineral free of that element, and samples of molybdenite should, therefore, be tested for the presence of copper.

The advantage obtained by applying the roasting process to molybdenite consists in freeing the mineral of the volatile bodies named, but that method involves a great outlay of money, since it necessitates the erection of a roasting furnace, which is a cumbersome and costly structure. As a rule, the introduction of such a furnace, which causes continuous expense in fuel and repair, should, therefore, be avoided if possible, as in this case, where the chemical method consisting of the treatment of the concentrates of molybdenite with nitric acid leads to the same final result. These concentrates can be obtained by using the Blake & Morscher electric separator on the ore, which, as judged by the Colorado species, seldom averages more than 10 per cent. The machine named will concentrate molybdenite ore of four, seven, and ten per cent. in almost all cases to eighty per cent. and more, the only exception observed having been a mineral which consisted in great part of conglomerated mica. In other cases where the country rock was quartz, or porphyritic quartz, the concentration of the ore to between 80 and 90 per cent. was effected by the machine with the greatest facility.

As a general characteristic for the habitat of molybdenite is to be mentioned, that it occurs, in Colorado at least, only at or above the timber line, and as a rule disseminated through the country rock in spots or bands, also in pockets, but rather seldom in real veins. As the ore is always low grade and found only in high altitudes, transportation to a manufacturing center should be avoided and the concentration effected in place. These machines of Blake & Morscher are of the double kind, being twenty-four feet in length, about four feet wide and seven feet high, and consume about 1 H. P. Being of an automatic character, ten of them can be operated and watched by one man, and this duty can be readily performed by the engine man. The separators named accomplish the concentration of the molybdenite from the gangue just as readily as the separation of zinc, iron and lead concentrates from the complex Leadville ores, eliminating besides in the latter case the silica in special parts. The molybdenite ore having been crushed to a 6 or 8 mesh, or other convenient size to loosen the metallic particles, one machine will handle between 12 and 15 tons in a day of twenty-four hours.

In case the chemical method is applied to the concentrates obtained by the work of these machines, the material to be treated is heated under the addition of nitric acid—the commercial article being employed in this case—when a violent reaction sets in accompanied by the emission of copious fumes of nitrogen dioxide, and the molybdenite is oxydized into molybdenum trioxide MoO_3, which separates out in form of a white thick mass, while iron oxide, generally present, enters into solution. The oxidation having been accomplished according to the equations:

$$\left\{\begin{array}{l} 2S+4HNO_3=2H_2SO_4+4NO \\ Mo+2HNO_3=MoO_3+2NO+H_2O, \end{array}\right.$$
$$\text{or}\quad MoS_2+6HNO_3=MoO_3+6NO+2H_2SO_4+H_2O,$$

the mass is allowed to cool, and carefully mixed with ammonia in slight excess, when the trioxide is completely dissolved, and the iron is precipitated from the solution as ferric hydrate. The latter having subsided, the clear supernant liquid, which now contains ammonium molybdate in solution, is siphoned or filtered from the solid remainder. Conditions are now as they were in the previous case, when the roasting process was applied, and the salt may be made to crystallize by evaporation. The ammonium molybdate obtained in this manner is either brought in the market as such, or subjected to roasting in a crucible, with continuous access of air, when it is decomposed first into the dioxide MoO_2 of a blue color and oxidized on further application of heat to the trioxide MoO_3, which is now of considerable purity, and wanted by the trade in general.

It sells in the retail trade when chemically pure and free of ammonia at $2 per pound, and the metal molybdenum at 40 cents per gram. The further purification of the trioxide, obtained as described above, can be effected by dissolving it again in ammonia, letting the molybdate crystallize, and decomposing the latter by the application of heat in a crucible.

It may then be mixed with carbon and reduced to metallic molybdenum or melted together with a good quality of iron, under the addition of charcoal, and thus worked into ferro-molybdenum. As stated before, the molybdenum steel, obtainable by the incorporation of the alloy with carbon steel, is claimed to possess properties which render it superior to tungsten steel. At least a comparison of molybdenum and tungsten steel, of which the former contained 3.7 per cent. of the alloying metal, and the latter 3.8 per cent.—both being else nearly equal in composition—showed that the molybdenum steel was somewhat the softer of the two, and that common tempering methods affected the tungsten steel more forcibly than the other. The molybdenum steel was, however, stronger and less brittle than the tungsten steel after heating and tempering in water, while tungsten steel was more apt to split when worked, and broke more easily when bent cold. It was also found that the molybdenum steel stood heat treatment the better of the two.

Since Krupp, the steel manufacturer of Essen, Germany, has been and is still buying large amounts of molybdenite, it is assumed that molybdenum is used extensively in his works for the preparation of superior steels, while it is an assured fact that English manufacturers of alloys deal largely in metallic molybdenum and ferro-molybdenum. As to the mode of manufacturing this steel the same experiment which was made with tungsten powder was made with molybdenum in powder form, inasmuch as the latter was found to float on the surface of the molten carbon steel, and to oxidize when introduced in that form. The ferro-alloy was, therefore, resorted to, and a compound prepared which carries 50, 70, 75 and 85 per cent. of metallic molybdenum, besides the iron, and is applied to the steel bath under the precaution of enclosing the calculated amount of the alloy in an iron tube before immersion.

This ferro-molybdenum steel was further improved by the introduction of various percentages of nickel, and a material obtained which more than answered expectations, since it was found to be readily fusible, the nickel acting as a vehicle. The great value of this ferro-nickel-molybdenum steel was readily acknowledged in this country as well as abroad, so that it is employed at present to a large extent in the United States, in England, and on the Continent. It serves principally for the manufacture of forgings, guns, rifle barrels, boiler plates and shells, and is found in the market as a compound, carrying about 75 per cent. molybdenum and 25 per cent. nickel, or nearly 50 per cent. molybdenum and 50 per cent. nickel, besides:

Iron	2.0 to 2.5 per cent.
Carbon	1.0 to 1.5 per cent.
Silicon	0.25 to 0.5 per cent.

Since molybdenum increases the elongation of carbon steel considerably and very much more so than nickel alone, the importance of this alloy will be easily recognized. It is added by leading firms in such proportion that the finished molybdenum-nickel steel contains 0.25 per cent. molybdenum, whereby the elongation of the steel is increased from 4 to 45 per cent. It will be readily seen then. that this effect of the alloy is of the greatest value for all classes of forgings, and particularly for large crank and propeller shafts. Since the addition of this small percentage of the alloy causes but little expense, it is evident also that an increase of elongation, obtained at such small cost, is of the greatest import for wire drawing, while experience shows that a molybdenum-nickel steel of that composition is a very desirable material for the manufacture of plates for high pressure boilers or boilers of torpedo boats.

Furthermore, it has been found that, by the addition of about 1 per cent. of molybdenum the hardest chrome-nickel steels are rendered readily machinable —a fact which is of great interest and importance to manufacturers of armor plates, shells and similar products. In order to show, however. the unusual activity displayed at present in this field of metallurgy, we will mention that a patent has been obtained lately, numbered 22,504. for a high grade steel. containing less than 1.20 per cent. of carbon. from 6 to 15 per cent. of molybdenum. from 2.50 to 6 per cent. of chromium. and less than 2 per cent. of silicon.

It must be emphasized, however. that the concentrates of molybdenite, as obtained by the Blake & Morscher separator, form by themselves a commercial product, which finds a ready market. The price paid for them depends upon the degree of concentration obtained, the usual concentrates of 80 per cent. molybdenite bringing about $300 per short ton, as long as they are free of copper.

In some cases the ore is partly oxidized into the yellow oxide, molybdite, which is removed from the concentrates by means of ammonia, which dissolves it and leaves the purified molybdenite behind. Whenever such favorable conditions exist, molybdenite concentrates, ammonium molybdate and the trioxide can be obtained without employing nitric acid, the manufacturing expenses being limited in this case to the outlay for ammonia and the production of the necessary heat for decomposing the ammonium molybdate into the trioxide.

When molybdenite is drawn over paper, it leaves a mark of greenish-gray color, very similar to that produced by graphite, and it is for this reason that the pure product is employed in the manufacture of pencils. Furthermore, it finds application as a lubricator for heavy work like graphite, but must be in this case entirely free of quartz or any other gangue. The salts of molybdenum are also highly estimated as producers of pigments, and are used for decorating china, and in the finer line of painting, and finally for the dyeing of silks and similar fabric.

ANALYTICAL METHODS.

(a)

Volumetric Determination of Uranium.

Reduction with zinc and subsequent titration with permanganate may be employed for the determination of uranium, but the solution must contain the sulphate or the acetate, and the point of complete reduction by the zinc is difficult to recognize. The safest way is, therefore, to dissolve the potassium salt, obtained according to the directions given on page 125. of "Analysis, Detection and Commercial Value of the Rare Metals," in dilute sulphuric or acetic acid, to introduce the zinc, let it act for at least half an hour, and then titrate the solution with permanganate to incipient redness.

The standard of the permanganate is found by titrating a weighed quantity of uranium sulphate or acetate in a similarly treated solution.

The formula of uranium sulphate is: UO_2SO_4; that of uranium acetate, $UO_2(C_2H_3O_2)_2H_2O$.

(b)

Determination of Molybdenum by Mercurous Nitrate.

Prepare the ammoniacal solution of the molybdic acid as described for tungstic acid on page 18, dilute it, neutralize the free ammonia with nitric acid, and after a few minutes' standing, add solution of c. p. mercurous nitrate. The yellow precipitate formed appears at first bulky, but after several hours it shrinks. It is insoluble in the fluid containing an excess of mercurous nitrate.

Collect the precipitate on a filter and wash with a dilute solution of mercurous nitrate, as it is slightly soluble in pure water. Dry, remove the precipitate as far as possible from the filter, ignite, mix the precipitate together with the filter-ash, with a weighed quantity of ignited lead oxide, and ignite under the hood, until all the mercury is expelled. Then add some ammonium nitrate, ignite again and weigh. The excess obtained, over and above the weight of the lead oxide used, is molybdenum trioxide MoO_3.

(c)

Determination of Tungsten by Mercurous Nitrate.

Having prepared the ammoniacal solution of the tungstic acid, as indicated on page 18, saturate the solution carefully with nitric acid, so that it will slightly redden litmus paper, let stand over night (24 hours) and add solution of mercurous nitrate as long as a precipitate is produced. Let the precipitate settle, collect it on a filter, and wash with water to which has been added a little mercurous nitrate. This operation is necessary to prevent the liquor from running through the filter turbid. After drying, incinerate the precipitate under a hood with a good draught. After calcination tungstic acid—WO_3—remains pure. Repeat the ignition to constant weight.

(d)

Determination of Vanadium.

Fuse the ore, which has been finely pulverized, with 15 per cent. sodium carbonate and 2 per cent. potassium nitrate for two hours in a fire-clay crucible in a muffle to a red heat, and lixiviate the mass. Filter, and to the filtrate add nitric acid, leaving the solution slightly alkaline. Filter, if necessary, and add to the filtrate barium chloride, so long as it produces a precipitate. Filter off the barium salts, and to the still moist precipitate add dilute sulphuric acid in slight excess, boil and filter. Then neutralize the filtrate with ammonia, concentrate, and add sal ammoniac in excess. As the ammonium chloride dissolves, ammonium metavanadate is precipitated in form of a crystalline powder. Allow it to settle, filter it off, and wash with solution of ammonium chloride. Dry the precipitate, and heat it to red vanadic oxide—V_2O_5—, which fuses, and cools to a crystalline mass.

(e)

Determination of Molybdenum as Barium Molybdate.

Weigh off one gram of the "finely pulverized" ore and dissolve it in "aqua regia," since nitric acid alone is only effective on repeated boiling. Take up with water containing some ammonium chloride to prevent the acid formed running through the pores of the filter. Now filter, wash with ammonium chloride water, until a drop of the filtrate gives no precipitate with barium chloride solution, and finally with alcohol. Dissolve the molybdic acid on the filter with solution of caustic potash, and neutralize the filtrate with nitric acid. The solution becomes colored deep green. Boil, add, while warm, a few drops of hydrogen peroxide, and drive off the excess of the latter by boiling. The solution turns yellow. Add barium chloride in solution to precipitate barium molybdate, which is filtered off, dried and weighed. From this calculate Mo.

K